APPENDIX D

MICROBIAL ANALYTICAL REPORTS

Lab Name	Sample Name	Sample Date	Date Received	Sample Matrix	LIMS Identifier	Extraction Date	Analysis Date	Analysis Method	Parameter	Result	Result Qualifier	Units	Detection Limit	Report Limit
MI	ST012-W11-WG-0714	7/16/2014	7/17/2014	Water	042LG-1	7/17/2014	7/23/2014	CENSUS	APS	3.76E+04	=	cells/mL	0.00E+00	0.00E+00
MI	ST012-W11-WG-0714	7/16/2014	7/17/2014	Water	042LG-1	7/17/2014	7/23/2014	CENSUS	GEO	8.94E+01	=	cells/mL	0.00E+00	0.00E+00
MI	ST012-W11-WG-0714	7/16/2014	7/17/2014	Water	042LG-1	7/17/2014	7/23/2014	CENSUS	MGN	5.73E+05	=	cells/mL	0.00E+00	0.00E+00
MI	ST012-W11-WG-0714	7/16/2014	7/17/2014	Water	042LG-1	7/17/2014	7/23/2014	CENSUS	nirK	2.26E+06	=	cells/mL	1.00E-01	4.60E+00
MI	ST012-W11-WG-0714	7/16/2014	7/17/2014	Water	042LG-1	7/17/2014	7/23/2014	CENSUS	nirS	1.34E+05	=	cells/mL	1.00E-01	4.60E+00
MI	ST012-W30-WG-0714	7/16/2014	7/17/2014	Water	042LG-2	7/17/2014	7/23/2014	CENSUS	MGN	5.05E+04	=	cells/mL	0.00E+00	0.00E+00
MI	ST012-W30-WG-0714	7/16/2014	7/17/2014	Water	042LG-2	7/17/2014	7/23/2014	CENSUS	APS	4.45E+04	=	cells/mL	0.00E+00	0.00E+00
MI	ST012-W30-WG-0714	7/16/2014	7/17/2014	Water	042LG-2	7/17/2014	7/23/2014	CENSUS	NIRK	8.06E+05	=	cells/mL	1.00E-01	4.50E+00
MI	ST012-W30-WG-0714	7/16/2014	7/17/2014	Water	042LG-2	7/17/2014	7/23/2014	CENSUS	NIRS	4.25E+05	=	cells/mL	1.00E-01	4.50E+00
MI	ST012-W30-WG-0714	7/16/2014	7/17/2014	Water	042LG-2	7/17/2014	7/23/2014	CENSUS	GEO	2.33E+01	=	cells/mL	0.00E+00	0.00E+00
MI	ST012-W11-WG-0714	7/17/2014	7/18/2014	Water	042LG-1	7/18/2014	7/29/2014	PLFA	Cells	28200	=	cells/mL	5.17E+03	1.72E+04
MI	ST012-W11-WG-0714	7/17/2014	7/18/2014	Water	042LG-1	7/18/2014	7/29/2014	PLFA	Firmicutes (TerBrSats)	34.68	=	%		
MI	ST012-W11-WG-0714	7/17/2014	7/18/2014	Water	042LG-1	7/18/2014	7/29/2014	PLFA	Proteobacteria (Monos)	33.82	=	%		
MI	ST012-W11-WG-0714	7/17/2014	7/18/2014	Water	042LG-1	7/18/2014	7/29/2014	PLFA	Anaerobic metal reducers (BrMonos)	1.68	=	%		
MI	ST012-W11-WG-0714	7/17/2014	7/18/2014	Water	042LG-1	7/18/2014	7/29/2014	PLFA	SRB/Actinomycetes (MidBrSats)	2.77	=	%		
MI	ST012-W11-WG-0714	7/17/2014	7/18/2014	Water	042LG-1	7/18/2014	7/29/2014	PLFA	General (Nsats)	27.06	=	%		
MI	ST012-W11-WG-0714	7/17/2014	7/18/2014	Water	042LG-1	7/18/2014	7/29/2014	PLFA	Eukaryotes (polyenoics)	0	ND	%		
MI	ST012-W11-WG-0714	7/17/2014	7/18/2014	Water	042LG-1	7/18/2014	7/29/2014	PLFA	Slowed Growth	0.966045	=	ratio cy/cis		
MI	ST012-W11-WG-0714	7/17/2014	7/18/2014	Water	042LG-1	7/18/2014	7/29/2014	PLFA	Decreased Permeability	0	ND	ratio trans/cis		
MI	ST012-W30-WG-0714	7/17/2014	7/18/2014	Water	042LG-2	7/18/2014	7/29/2014	PLFA	Cells	57500	=	cells/mL	2.74E+03	9.14E+03
MI	ST012-W30-WG-0714	7/17/2014	7/18/2014	Water	042LG-2	7/18/2014	7/29/2014	PLFA	Firmicutes (TerBrSats)	48.44	=	%		
MI	ST012-W30-WG-0714	7/17/2014	7/18/2014	Water	042LG-2	7/18/2014	7/29/2014	PLFA	Proteobacteria (Monos)	22.59	=	%		
MI	ST012-W30-WG-0714	7/17/2014	7/18/2014	Water	042LG-2	7/18/2014	7/29/2014	PLFA	Anaerobic metal reducers (BrMonos)	5.4	=	%		
MI	ST012-W30-WG-0714	7/17/2014	7/18/2014	Water	042LG-2	7/18/2014	7/29/2014	PLFA	SRB/Actinomycetes (MidBrSats)	3.99	=	%		
MI	ST012-W30-WG-0714	7/17/2014	7/18/2014	Water	042LG-2	7/18/2014	7/29/2014	PLFA	General (Nsats)	19.6	=	%		
MI	ST012-W30-WG-0714	7/17/2014	7/18/2014	Water	042LG-2	7/18/2014	7/29/2014	PLFA	Eukaryotes (polyenoics)	0	ND	%		
MI	ST012-W30-WG-0714	7/17/2014	7/18/2014	Water	042LG-2	7/18/2014	7/29/2014	PLFA	Slowed Growth	0.902733	=	ratio cy/cis		
MI	ST012-W30-WG-0714	7/17/2014	7/18/2014	Water	042LG-2	7/18/2014	7/29/2014	PLFA	Decreased Permeability	0.118881	=	ratio trans/cis		

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865-573-8188

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REPORT TO:

Name: Amec E&I
Company: Amec E&I
Address: 511 Congress St. Portland, ME 04101

email: stuart.pearson@amec.com
Phone: 207-828-3479
Fax: 207-772-4762

INVOICE TO: (For invoices paid by a third party it is imperative that all information be provided)

Name:
Company:
Address:

email:
Phone:
Fax:

Project Manager: Stu Pearson
Project Name: FWAFB ST012 EBR
Project No.: 9101110001.5300.5301

Purchase Order No. F014200244
Subcontract No.
MI Quote No. Q 201471.0001

Please Check One:
☒ More samples to follow
☐ No Additional Samples

Report Type: ☐ Standard (default) ☐ Microbial Insights Level III raw data(15% surcharge) ☐ Microbial Insights Level IV (25% surcharge) ☐ Comprehensive Interpretive(15%) ☐ Historical Interpretive (35%)

EDD type: ☐ Microbial Insights Standard (default) ☐ All other available EDDs (5% surcharge) Specify EDD Type: ______

Please contact us with any questions about the analyses or filling out the COC at (865) 573-8188 (9:00 am to 5:00 pm EST, M-F). After hours email: customerservice@microbe.com

Sample Information					Analyses					CENSUS: Please select the target organism/gene																							
MI ID (Laboratory Use Only)	Sample Name	Date Sampled	Time Sampled	Matrix	~~PLFA~~	DGGE+3ID	DGGE+6ID	QuantArray Chlor	QuantArray Petro	DHC (Dehalococcoides)	DHC Functional genes (tce, bvc, vcr)	DHB (Dehalobacter)	DSM (Desulfuromonas)	DSB (Desulfitobacterium)	EBAC (Total)	SRB (Sulfate Reducing Bacteria-APS)	MGN (Methanogens)	MOB (Methanotrophs)	SMMO	DNF (Denitrifiers-nirS and nirK)	AOB (Ammonia oxidizing bacteria)	PM1 (MTBE aerobic)	RMO (Toluene Monooxygenase)	RDEG (Toluene Monooxygenase)	PHE (Phenol Hydroxylase)	NAH (Naphthalene aerobic)	BSSA (Toluene/Xylene Anaerobic)	qPCR	qPCR	RNA (Expression Option)*	Other: Geobacter spp (G)	Other	Other
042LG1	ST012-W11-WG-0714	7/16/14	1245	W	~~X~~											X	X			X											X		
2	ST012-W30-WG-0714	7/16/14	1515	W	~~✓~~											X	X			X											X		

Note: Additional bottles to run the PLFA SAMPLES will be submitted 7/18 (samples collected 7/17).

Relinquished by: Shanda Lwy | Received by: [signature] | Date 7/16/14 | 7/17/14

It is vital that chain of custody is filled out correctly & that all relative information is provided.
Failure to provide sufficient and/or correct information regarding reporting, invoicing & analyses requested information may result in delays for which MI will not be liable.

* additional cost and sample preservation are associated with RNA samples.

**Saturday delivery: See sampling protocol for alternate shipping address.

REPORT TO:

Name: Amec E & I
Company: Amec E&I
Address: 511 Congress St.
Portland, ME 04101

email: stuart.pearson@amec.com
Phone: 207-828-3479
Fax: 207-772-4762

Project Manager: Stu Pearson
Project Name: FWAFB ST012 EBR
Project No.: 910111 0001.5300.5301

INVOICE TO: (For invoices paid by a third party it is imperative that all information be provided)

Name:
Company:
Address:

email:
Phone:
Fax:

Purchase Order No. F014200244
Subcontract No.
MI Quote No. Q 2014 71.0001

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Please Check One:
☒ More samples to follow
☐ No Additional Samples

Report Type: ☐ Standard (default) ☐ Microbial Insights Level III raw data(15% surcharge) ☐ Microbial Insights Level IV (25% surcharge) ☐ Comprehensive Interpretive(15%) ☐ Historical Interpretive (35%)

EDD type: ☐ Microbial Insights Standard (default) ☐ All other available EDDs (5% surcharge) Specify EDD Type:

Please contact us with any questions about the analyses or filling out the COC at (865) 573-8188 (8:00 am to 5:00 pm EST, M-F). After hours email: customerservice@microbe.com

Sample Information					Analyses				
MI ID (Laboratory Use Only)	Sample Name	Date Sampled	Time Sampled	Matrix	PLFA	DGGE+3ID	DGGE+5ID	QuantArray Chlor	QuantArray Petro
042LG1	ST012-W11-WG-0714	7/16/14	1245	W	X				
2	ST012-W30-WG-0714	7/16/14	1515	W	X				
	ST012-W11-WG-0714	7/17/14	14:10	W	X				
	ST012-W30-WG-0714	7/17/14	10:00	W	X				

CENSUS: Please select the target organism/gene

Sample Name	DHC (Dehalococcoides)	DHC Functional Genes (tceA, bvcA, vcrA)	DHBt (Dehalobacter)	DSM (Desulfuromonas)	DSB (Desulfitobacterium)	EBAC (Total)	SRB (Sulfate Reducing Bacteria APS)	MGN (Methanogens)	MOB (Methanotrophs)	SMMO	DNF (Denitrifiers nirS and nirK)	AOB (ammonia oxidizing bacteria)	PM1 (MTBE aerobic)	RMO (Toluene Monooxygenase)	RDEG (Toluene Monooxygenase)	PHE (Phenol Hydroxylase)	NAH (Naphthalene-aerobic)	BSSA (Toluene/Xylene Anaerobic)	qPCR	qPCR	RNA (Expression Option)*	Other: Geobacter SIP Geo	Other	Other
ST012-W11-WG-0714 (7/16/14)							X	X			X											X		
ST012-W30-WG-0714 (7/16/14)							X	X			X											X		

Note: Additional bottles to run the PLFA samples will be submitted 7/18 (samples collected 7/17).

Please use these to run PLFA Analysis

Relinquished by: Shanda Lopez / Shanda LeWas Received by: [signature] Date 7/16/14 / 7/17/14 7/18/14

It is vital that chain of custody is filled out correctly & that all relative information is provided. Failure to provide sufficient and/or correct information regarding reporting, invoicing & analyses requested information may result in delays for which MI will not be liable.

* additional cost and sample preservation are associated with RNA samples.

**Saturday delivery: See sampling protocol for alternate shipping address.

Lab Name	Sample Name	Sample Date	Date Received	Sample Matrix	LIMS Identifier	Extraction Date	Analysis Date	Analysis Method	Parameter	Result	Result Qualifier	Units	Detection Limit	Report Limit
MI	ST012-W11-WG-0714	7/16/2014	7/17/2014	Water	042LG-1	7/17/2014	7/23/2014	CENSUS	APS	3.76E+04	=	cells/mL	0.00E+00	0.00E+00
MI	ST012-W11-WG-0714	7/16/2014	7/17/2014	Water	042LG-1	7/17/2014	7/23/2014	CENSUS	GEO	8.94E+01	=	cells/mL	0.00E+00	0.00E+00
MI	ST012-W11-WG-0714	7/16/2014	7/17/2014	Water	042LG-1	7/17/2014	7/23/2014	CENSUS	MGN	5.73E+05	=	cells/mL	0.00E+00	0.00E+00
MI	ST012-W11-WG-0714	7/16/2014	7/17/2014	Water	042LG-1	7/17/2014	7/23/2014	CENSUS	nirK	2.26E+06	=	cells/mL	1.00E-01	4.60E+00
MI	ST012-W11-WG-0714	7/16/2014	7/17/2014	Water	042LG-1	7/17/2014	7/23/2014	CENSUS	nirS	1.34E+05	=	cells/mL	1.00E-01	4.60E+00
MI	ST012-W30-WG-0714	7/16/2014	7/17/2014	Water	042LG-2	7/17/2014	7/23/2014	CENSUS	MGN	5.05E+04	=	cells/mL	0.00E+00	0.00E+00
MI	ST012-W30-WG-0714	7/16/2014	7/17/2014	Water	042LG-2	7/17/2014	7/23/2014	CENSUS	APS	4.45E+04	=	cells/mL	0.00E+00	0.00E+00
MI	ST012-W30-WG-0714	7/16/2014	7/17/2014	Water	042LG-2	7/17/2014	7/23/2014	CENSUS	NIRK	8.06E+05	=	cells/mL	1.00E-01	4.50E+00
MI	ST012-W30-WG-0714	7/16/2014	7/17/2014	Water	042LG-2	7/17/2014	7/23/2014	CENSUS	NIRS	4.25E+05	=	cells/mL	1.00E-01	4.50E+00
MI	ST012-W30-WG-0714	7/16/2014	7/17/2014	Water	042LG-2	7/17/2014	7/23/2014	CENSUS	GEO	2.33E+01	=	cells/mL	0.00E+00	0.00E+00

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Client:	Stuart Pearson AMEC E & I, Inc. 511 Congress Street Portland, ME 04101	**Phone:** **Fax:**	

Identifier: 042LG **Date Rec:** 07/17/2014 **Report Date:** 07/24/2014

Client Project #: 9101110001.5300.5301 **Client Project Name:** FWAFB ST012 EBR

Purchase Order #: F014200244

Analysis Requested: CENSUS, PLFA

Reviewed By:

MICROBIAL INSIGHTS, INC.

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CENSUS

Client: **AMEC E & I, Inc.**
Project: FWAFB ST012 EBR

MI Project Number: **042LG**
Date Received: 07/17/2014

Sample Information

Client Sample ID:		**ST012-W11-WG -0714**	**ST012-W30-WG -0714**
Sample Date:		07/16/2014	07/16/2014
Units:		cells/mL	cells/mL
Analyst:		RW	RW
Functional Genes			
Denitrifying Bacteria	nirK	**2.26E+06**	**8.06E+05**
Denitrifying Bacteria	nirS	**1.34E+05**	**4.25E+05**
Other Genera			
Geobacter spp.	*GEO*	**8.94E+01**	**2.33E+01**
Phylogenetic Group			
Sulfate Reducing Bacteria	APS	**3.76E+04**	**4.45E+04**
Methanogen	MGN	**5.73E+05**	**5.05E+04**

Legend:
NA = Not Analyzed NS = Not Sampled J = Estimated gene copies below PQL but above LQL I = Inhibited
< = Result not detected

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Client: Stuart Pearson
AMEC E & I, Inc.
511 Congress Street
Portland, ME 04101

Phone:

Fax:

Identifier: 042LG **Date Rec:** 07/17/2014 **Report Date:** 07/29/2014

Client Project #: 9101110001.5300.5301 **Client Project Name:** FWAFB ST012 EBR

Purchase Order #: F014200244

Analysis Requested: CENSUS, PLFA

Reviewed By:

Kate Clark

MICROBIAL INSIGHTS, INC.

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PLFA

Client:	**AMEC E & I, Inc.**	**MI Project Number:**	**042LG**
Project:	FWAFB ST012 EBR	Date Received:	07/17/2014

Sample Information

Sample Name:	**ST012-W11-WG-0714**	**ST012-W30-WG-0714**
Sample Date:	07/17/2014	07/17/2014
Sample Matrix:	Water	Water
Analyst:	BJ	BJ

Biomass

Total Biomass (cells/mL)	**2.82E+04**	**5.75E+04**

Community Structure (% total PLFA)

Firmicutes (TerBrSats)	**34.68**	**48.44**
Proteobacteria (Monos)	**33.82**	**22.59**
Anaerobic metal reducers (BrMonos)	**1.68**	**5.40**
SRB/Actinomycetes (MidBrSats)	**2.77**	**3.99**
General (Nsats)	**27.06**	**19.60**
Eukaryotes (polyenoics)	**0.00**	**0.00**

Physiological Status (Proteobacteria only)

Slowed Growth	**0.97**	**0.90**
Decreased Permeability	**0.00**	**0.12**

Legend:
NA = Not Analyzed NS = Not Sampled

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PLFA

Client: **AMEC E & I, Inc.**
Project: FWAFB ST012 EBR

MI Project Number: **042LG**
Date Received: 07/17/2014

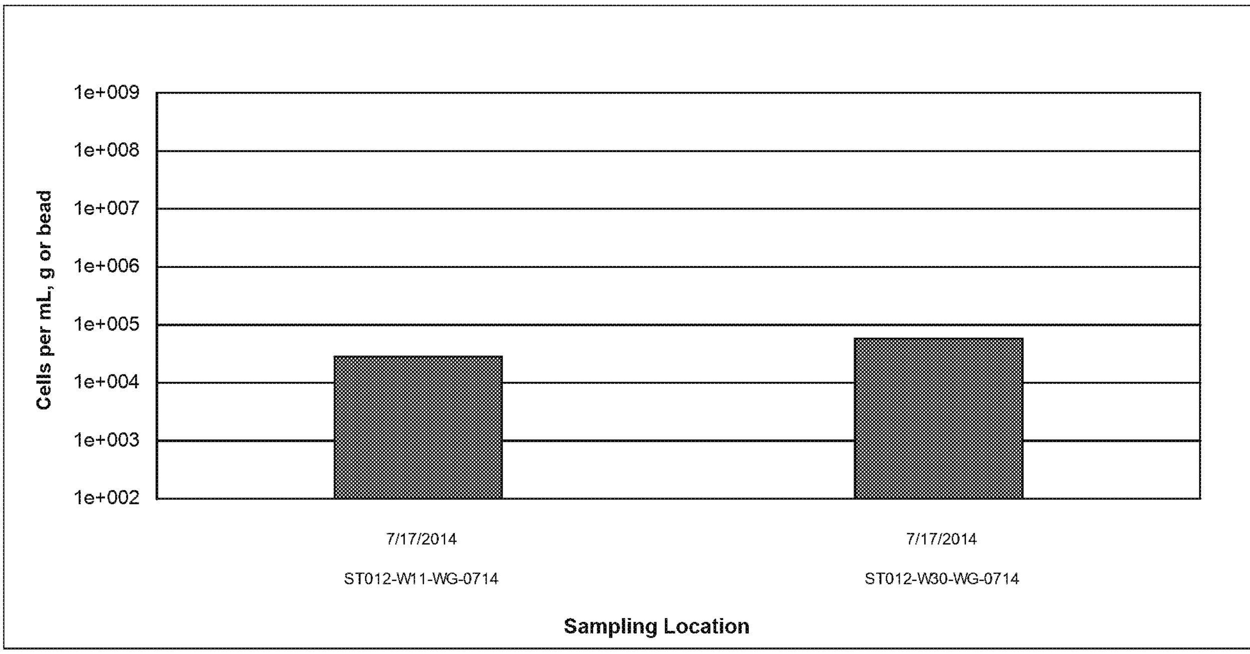

Figure 1. Biomass content is presented as a cell equivalent based on the total amount of phospholipid fatty acids (PLFA) extracted from a given sample. Total biomass is calculated based upon PLFA attributed to bacterial and eukaryotic biomass

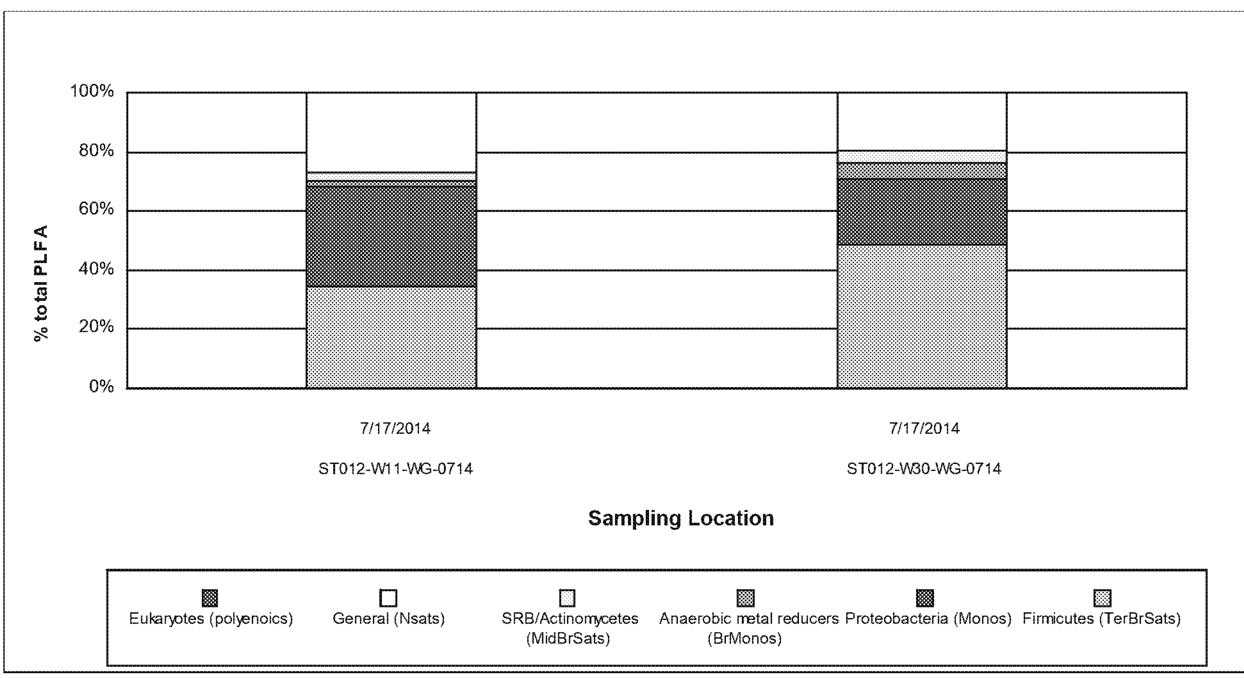

Figure 2. Relative percentages of total PLFA structural groups in the samples analyzed. Structural groups are assigned according to PLFA chemical structure, which is related to fatty acid biosynthesis.

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Phospholipid Fatty Acid Analysis

Interpretation Guidelines

Phospholipids fatty acids (PLFA) are a main component of the membrane (essentially the "skin") of microbes and provide a powerful tool for assessing microbial responses to changes in their environment. This type of analysis provides direct information for assessing and monitoring sites where bioremediation processes, including natural attenuation, are of interest. Analysis of the types and amount of PLFA provides a broad based understanding of the entire microbial community with information obtained in three key areas viable biomass, community structure and metabolic activity.

What is the detection limit for PLFA?

Our limit of detection for PLFA analysis is ~150 picomoles of total PLFA and our limit of quantification is ~500 picomoles of total PLFA. Samples which contain PLFA amounts at or below 150 pmol cannot be used to determine biomass, likewise samples with PLFA content below ~500 pmol are generally considered to contain too few fatty acids to discuss community composition.

How should I interpret the PLFA results?

Interpreting the results obtained from PLFA analysis can be somewhat difficult, so this document was designed to provide a technical guideline. For convenience, this guideline has been divided into the three key areas.

Viable Biomass

PLFA analysis is one of the most reliable and accurate methods available for the determination of viable microbial biomass. Phospholipids break down rapidly upon cell death (21, 23), so biomass calculations based on PLFA content do not contain 'fossil' lipids of dead cells.

How is biomass measured?

Viable biomass is determined from the total amount of PLFA detected in a given sample. Since, phospholipids are an essential part of intact cell membranes they provide an accurate measure of viable cells.

How is biomass calculated?

Biomass levels are reported as cells per gram, mL or bead, and are calculated using a conversion factor of 20,000 cells/pmole of PLFA. This conversation factor is based upon cells grown in laboratory media, and varies somewhat with the type of organism and environmental conditions.

What does the concentration of biomass mean?

The overall abundance of microbes within a given sample is often used as an indicator of the potential for bioremediation to occur, but understanding the levels of biomass within each sample can be cumbersome. The following are benchmarks that can be used to understand whether the biomass levels are low, moderate or high.

Low	Moderate	High
10^3 to 10^4 cells	10^5 to 10^6 cells	10^7 to 10^8 cells

How do I know if a change in biomass is significant?

One of the primary functions of using PLFA analysis at contaminated sites is to evaluate how a community responds following a given treatment, but how does one know if the changes observed between two events are significant? As a general rule, biomass levels which increase or decrease by at least an order of magnitude are considered to be significant. However, changes in biomass levels of less than an order of magnitude may still show a trend. It is important to remember that many factors can affect microbial growth, so factors other than the treatment could be influencing the changes observed between sampling events. Some of the factors to consider are: temperature, moisture, pH, etc. The following illustration depicts three types of changes that occurred over time and the conclusions that could be drawn.

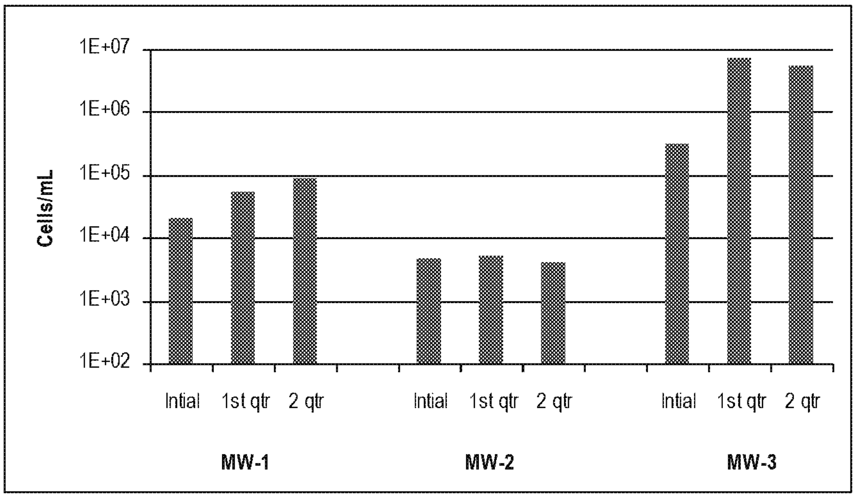

Figure 1. Biomass content is presented as a cell equivalent based on the total amount of phospholipid fatty acids (PLFA) extracted from a given sample. Total biomass is calculated based upon PLFA attributed to bacterial and eukaryotic biomass (associated with higher organisms).

Conclusions from graph above:

- MW-1 showed a trend of biomass levels increasing steadily over time, although cell concentrations were ~10^4 cells/mL at each sampling event.
- MW-2 showed no notable trends or significant changes in biomass concentrations.
- MW-3 showed a significant increase in biomass levels between the initial and 1st quarter sampling events (from ~10^5 to ~10^6 cells/mL).

Community Structure:

The PLFA in a sample can be separated into particular types, and the resulting PLFA "profile" reflects the proportions of the categories of organisms present in the sample. Because groups of bacteria differ in their metabolic capabilities, determining which bacterial groups are present and their relative distributions within the community can provide information on what metabolic processes are occurring at that location. This in turn can also provide information on the subsurface conditions (i.e oxidation/reduction status, etc.). Table 1 describes the six major structural groups used and their potential relevance to site specific projects.

Table 1. Description of PLFA structural groups.

PLFA Structural Group	General classification	Potential Relevance to Bioremediation Studies
Monoenoic (Monos)	Abundant in Proteobacteria (Gram negative bacteria), typically fast growing, utilize many carbon sources, and adapt quickly to a variety of environments.	Proteobacteria is one of the largest groups of bacteria and represents a wide variety of both aerobes and anaerobes. The majority of Hydrocarbon utilizing bacteria fall within the Proteobacteria
Terminally Branched Saturated (TerBrSats)	Characteristic of Firmicutes (Low G+C Gram-positive bacteria), and also found in Bacteriodes, and some Gram-negative bacteria (especially anaerobes).	Firmicutes are indicative of presence of anaerobic fermenting bacteria (mainly *Clostridia/Bacteriodes*-like), which produce the H_2 necessary for reductive dechlorination
Branched Monoenoic (BrMonos)	Found in the cell membranes of micro-aerophiles and anaerobes, such as sulfate- or iron-reducing bacteria	In contaminated environments high proportions are often associated with anaerobic sulfate and iron reducing bacteria
Mid-Chain Branched Saturated (MidBrSats)	Common in sulfate reducing bacteria and also Actinobacteria (High G+C Gram-positive bacteria).	In contaminated environments high proportions are often associated with anaerobic sulfate and iron reducing bacteria
Normal Saturated (Nsats)	Found in all organisms.	High proportions often indicate less diverse populations.
Polyenoic	Found in eukaryotes such as fungi, protozoa, algae, higher plants, and animals.	Eukaryotic scavengers will often rise up and prey on contaminant utilizing bacteria

Following are answers to some of the common questions about community composition and some detailed descriptions of some typical shifts which can be observed between sampling events.

How is the community structure data presented?

Community structure data is presented as percentage (%) of the total amount of PLFA. In order to relate the complex mixture of PLFA to the organisms present, the ratio of a specific PLFA group is determined (detailed in Table 1 above), and this corresponds to the proportion of the related bacterial classification within the overall community structure. Because normal saturated PLFA are found in both prokaryotes (bacteria) and eukaryotes (fungi, protozoa, diatoms etc), their distribution provides little insight into the types of microbes that are present at a sampling location. However, high proportions of normal saturates are often associated with less diverse microbial populations.

How can community structure data be used to manage my site?

It is important to understand that microbial communities are often a mixture of different types of bacteria (e.g. aerobes, sulfate reducers, methanogens, etc) with the abundance of each group behaving like a seesaw, i.e. as the population of one group increases, another is likely decreasing, mostly due to competition for available resources. The PLFA profile of a sample provides a "fingerprint" of the microbial community, showing relative proportions of the specific bacterial types at the time of sampling. This is a great tool for detecting shifts within the community over time and also to evaluate similarities/differences between sampling locations. It is important to note that PLFA analysis of community structure is analyzing the microbes directly, not just secondary breakdown products. So this provides evidence of how the entire microbial community is responding to the treatment.

How do I recognize community shifts and what they mean?

Shifts in the community structure are indications of changing conditions and their effect on the microbial community, and, by extension on the metabolic processes occurring at the sampling location. Some of the more commonly seen shifts within the community are illustrated and discussed below:

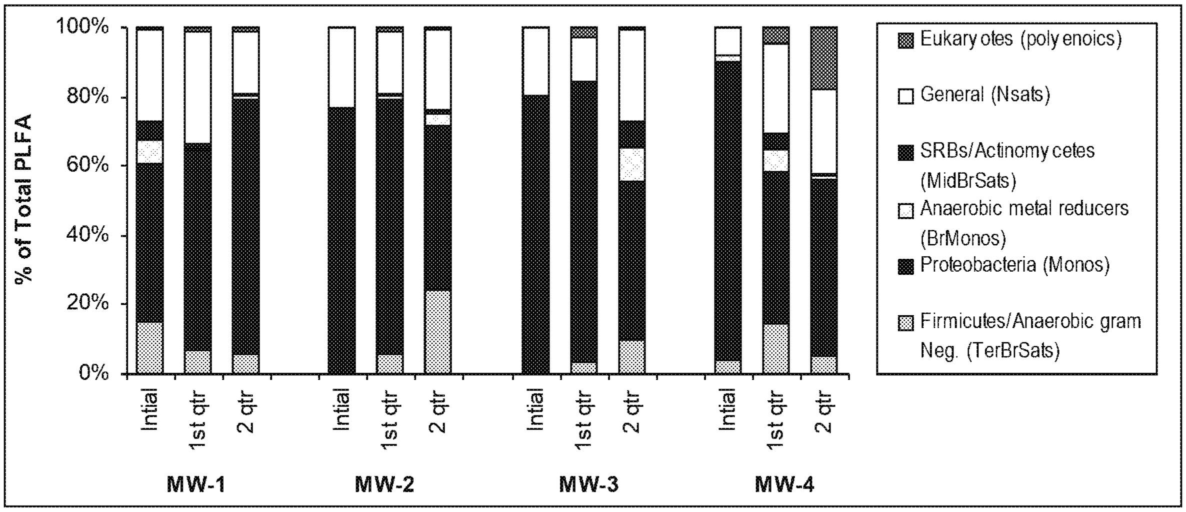

Figure 2. Relative percentages of total PLFA structural groups in the samples analyzed. Structural groups are assigned according to PLFA chemical structure, which is related to fatty acid biosynthesis. See Table 1 for detailed descriptions of structural groups.

- **Increased Proteobacteria**

Proportions of Proteobacteria are of interest because it is one of the largest groups of bacteria and represents a wide variety of both aerobe and anaerobes. The majority of hydrocarbons (including benzene and naphthalene) are metabolized by some member of Proteobacteria, mainly due to their ability to grow opportunistically, quickly taking advantage of available food (i.e. hydrocarbons), and adapting quickly to changes in the environment. The detection of increased proportions of Proteobacteria coupled with increased biomass suggests that the Proteobacteria are consuming something. In situations where it is important to determine the extent to which the Proteobacteria are utilizing anaerobic or aerobic pathways, it is possible to measure relative proportions of specific biomarkers that are associated with anaerobic or aerobic pathways thus separating the Proteobacteria into different groups, based on pathways used. Sample MW-1 from Figure 2 depicts a shift in community structure where the proportion of Proteobacteria has increased over time.

- **Increased Firmicutes/Anaerobic Gram negative bacteria**

Increased proportions of Firmicutes/Anaerobic Gram negative bacteria generally indicate that conditions are becoming more reductive (i.e. more anaerobic). Proportions of Firmicutes are of particular interest in sites contaminated with chlorinated hydrocarbons because Firmicutes include anaerobic fermenting bacteria (mainly *Clostridia/Bacteriodes*-like), which produce the H_2 necessary for reductive dechlorination.

Enhanced bioremediation of chlorinated solvents often employs the injection of fermentable substrates which, when utilized by fermenting bacteria, results in the release of H_2. Engineered shifts in the microbial community can be shown by observing increased proportions Firmicutes following an injection of fermentable substrate. Through long-term monitoring of the community structure it is possible to know when re-injection may be necessary or desirable. Sample MW-2 from Figure 2 depicts a shift in community structure where the proportion of Firmicutes has increased over time.

- **Increased anaerobic metal reducing bacteria (BrMonos) and SRB/Actinomycetes (MidBrSats)**

An increase in the proportions of metal and sulfate reducing bacterial groups, especially when combined with shifts in the other bacterial groups, can provide information helpful to monitoring bioremediation. Generally, an increase in metal and sulfate reducers points to more reduced (anaerobic) conditions at the sampled location. This is especially true if there is an increase in Firmicutes at the same time. Large increases in either metal and sulfate reducers, particularly if accompanied by a decrease in Firmicutes, may suggest that conditions are becoming increasingly reduced. In this situation the metal and sulfate reducers may be out-competing dechlorinators for available H_2, thereby limiting the potential for reductive dechlorination at that location. Sample MW-3 from Figure 2 depicts a shift in community structure where the proportion of metal reducing bacteria has increased over time.

- **Increased Eukaryotes**

Eukaryotes include organisms such as fungi, protozoa, and diatoms. At a contaminated location, an increase in eukaryotes, particularly if seen with a decrease in the contaminant utilizing bacteria, suggests that eukaryotic scavengers are preying upon what had been an abundance of bacteria which were consuming the contaminant. Sample MW-4 from Figure 2 depicts a shift in community structure where the proportion of eukaryotes has increased over time.

Physiological status of Proteobacteria

The membrane of a microbe adapts to the changing conditions of its environment, and these changes are reflected in the PLFA. Toxic compounds or environmental conditions may disrupt the membrane and some bacteria respond by making *trans* fatty acids instead of the usual *cis* fatty acids (7) in order to strengthen the cell membrane, making it less permeable. Many Proteobacteria respond to lack of available substrate or to highly toxic conditions by making cyclopropyl (7) or mid-chain branched fatty acids (20) which point to less energy expenditure and a slowed growth rate. The physiological status ratios for Decreased Permeability (trans/cis ratio) and for Slowed Growth (cy/cis ratio) are based on dividing the amount of the fatty acid induced by environmental conditions by the amount of its biosynthetic precursor.

What does slowed growth or decreased permeability mean?

Ratios for slowed growth and for decreased permeability of the cell membrane provide information on the "health" of the Gram negative community, that is, how this population is responding to the conditions present in the environment. It should be noted that one must be cautious when interpreting these measures from only one sampling event. The most effective way to use the physiological status indicators is in long term monitoring and comparing how these ratios increase/decrease over time.

A marked increase in either of these ratios suggests a change in environment which is less favorable to the Gram negative Proteobacteria population. The ratio for slowed growth is a relative measure, and does not directly correspond to log or stationary phases of growth, but is useful as a comparison of growth rates among sampling locations and also over time. An increase in this ratio (i.e. slower growth rate) suggests a change in conditions which is not as supportive of rapid, "healthy" growth of the Gram negative population, often due to reduced available substrate (food). A larger ratio for decreased permeability suggests that the environment has become more toxic to the Gram negative population, requiring energy expenditure to produce *trans* fatty acids in order to make the membrane more rigid.

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Lab Name	Sample Name	Sample Date	Date Received	Sample Matrix	LIMS Identifier	Extraction Date	Analysis Date	Analysis Method	Parameter	Result	Result Qualifier	Units	Detection Limit	Report Limit
MI	STO12-W30-WG-090214	9/2/2014	9/3/2014	Water	002LI-1	9/4/2014	9/9/2014	CENSUS	APS	4.37E+04	=	cells/mL	0.00E+00	0.00E+00
MI	STO12-W30-WG-090214	9/2/2014	9/3/2014	Water	002LI-1	9/4/2014	9/9/2014	CENSUS	GEO	1.06E+04	=	cells/mL	0.00E+00	0.00E+00
MI	STO12-W30-WG-090214	9/2/2014	9/3/2014	Water	002LI-1	9/4/2014	9/9/2014	CENSUS	MGN	6.42E+04	=	cells/mL	1.00E-01	4.50E+00
MI	STO12-W30-WG-090214	9/2/2014	9/3/2014	Water	002LI-1	9/4/2014	9/9/2014	CENSUS	nirK	4.89E+05	=	cells/mL	1.00E-01	4.50E+00
MI	STO12-W30-WG-090214	9/2/2014	9/3/2014	Water	002LI-1	9/4/2014	9/9/2014	CENSUS	nirS	3.20E+04	=	cells/mL	1.00E-01	4.50E+00
MI	STO12-W11-WG-090214	9/2/2014	9/3/2014	Water	002LI-2	9/3/2014	9/9/2014	CENSUS	GEO	1.53E+04	=	cells/mL	0.00E+00	0.00E+00
MI	STO12-W11-WG-090214	9/2/2014	9/3/2014	Water	002LI-2	9/3/2014	9/9/2014	CENSUS	APS	6.49E+05	=	cells/mL	0.00E+00	0.00E+00
MI	STO12-W11-WG-090214	9/2/2014	9/3/2014	Water	002LI-2	9/3/2014	9/9/2014	CENSUS	MGN	7.00E+04	=	cells/mL	1.00E-01	4.70E+00
MI	STO12-W11-WG-090214	9/2/2014	9/3/2014	Water	002LI-2	9/3/2014	9/9/2014	CENSUS	nirK	4.52E+05	=	cells/mL	1.00E-01	4.70E+00
MI	STO12-W11-WG-090214	9/2/2014	9/3/2014	Water	002LI-2	9/3/2014	9/9/2014	CENSUS	nirS	1.93E+04	=	cells/mL	1.00E-01	4.70E+00

REPORT TO:

Name: AMEC E&I

Company: 4600 E WASHINGTON STREET

Address: SUITE 600

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INVOICE TO: (For invoices paid by a third party it is imperative that all information be provided)

Name:

Company:

Address:

email:

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Fax:

mi microbialinsights

10515 Research Dr

Knoxville, TN 37932

865-573-8188

www.microbe.com

Project Manager: NATALIE CHRISMAN

Project Name: WAFB-ST012

Project No.: 9101110001.5300.5301

Purchase Order No.

Subcontract No.

MI Quote No.

Please Check One:

☐ More samples to follow

☐ No Additional Samples

Report Type: ☐ Standard (default) ☐ Microbial Insights Level III raw data(15% surcharge) ☐ Microbial Insights Level IV (25% surcharge) ☐ Comprehensive Interpretive(15%) ☐ Historical Interpretive (35%)

EDD type: ☐ Microbial Insights Standard (default) ☐ All other available EDDs (5% surcharge) Specify EDD Type:

Please contact us with any questions about the analyses or filling out the COC at (865) 573-8188 (9:00 am to 5:00 pm EST, M-F). After hours email: customerservice@microbe.com

Sample Information					Analyses					CENSUS: Please select the target organism/gene																							
MI ID (Laboratory Use Only)	Sample Name	Date Sampled	Time Sampled	Matrix	PLFA	DGGE+3ID	DGGE+5ID	QuantArray Chlor	QuantArray Petro	DHC (Dehalococcoides)	DHC Functional genes (tce, bvc, vcr)	DHBt (Dehalobacter)	DSM (Desulfuromonas)	DSB (Desulfitobacterium)	EBAC (Total)	SRB (Sulfate Reducing Bacteria-APS)	MGN (Methanogens)	MOB (Methanotrophs)	SMMO	DNF (Denitrifiers-nirS and nirK)	AOB (ammonia oxidizing bacteria)	PM1 (MTBE aerobic)	RMO (Toluene Monooxygenase)	RDEG (Toluene Monooxygenase)	PHE (Phenol Hydroxylase)	NAH (Napthalene-aerobic)	BSSA (Toluene/Xylene-Anaerobic)	add. qPCR:	add. qPCR:	RNA (Expression Option)*	Other: Geobacter SP	Other:	Other:
002LI 1	ST012-W30-W6-090214		10:37	AQ	X											X	X			X											X		
2	ST012-W11-W6-090214		13:40	↓	X											X	X			X											X		

Relinquished by: Eri Miller

Received by: Judith Clark

Date 9/3/14

It is vital that chain of custody is filled out correctly & that all relative information is provided.

Failure to provide sufficient and/or correct information regarding reporting, invoicing & analyses requested information may result in delays for which MI will not be liable.

* additional cost and sample preservation are associated with RNA samples.

**Saturday delivery: See sampling protocol for alternate shipping address.

REPORT TO:		**INVOICE TO:** (For invoices paid by a third party it is imperative that all information be provided)	
Name:	AMEC E&I / Stu Pearson	Name:	
Company:	AMEC E&I	Company:	
Address:	511 Congress St. Portland, ME 04101	Address:	
email:	stuart.pearson@amec.com	email:	
Phone:	207-828-3479	Phone:	
Fax:	207-772-4762	Fax:	
Project Manager:	Stu Pearson	Purchase Order No.	F01420024 4
Project Name:	FWAFB ST012 EBR	Subcontract No.	
Project No.:	9101110001.5300.5301	MI Quote No.	Q 201471.0001

microbial insights

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Please Check One:
☐ More samples to follow
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Report Type: ☐ Standard (default) ☐ Microbial Insights Level III raw data(15% surcharge) ☐ Microbial Insights Level IV (25% surcharge) ☐ Comprehensive Interpretive(15%) ☐ Historical Interpretive (35%)

EDD type: ☐ Microbial Insights Standard (default) ☐ All other available EDDs (5% surcharge) Specify EDD Type: ____________

Please contact us with any questions about the analyses or filling out the COC at (865) 573-8188 (9:00 am to 5:00 pm EST, M-F). After hours email: customerservice@microbe.com

Sample Information					Analyses					CENSUS: Please select the target organism/gene																						
MI ID (Laboratory Use Only)	Sample Name	Date Sampled	Time Sampled	Matrix	PLFA	DGGE+3ID	DGGE+5ID	QuantArray Chlor	QuantArray Petro	DHC (Dehalococcoides)	DHC Functional genes (tce, bvc, vcr)	DHBt (Dehalobacter)	DSM (Desulfuromonas)	DSB (Desulfitobacterium)	EBAC (Total)	SRB (Sulfate Reducing Bacteria-APS)	MGN (Methanogens)	MOB (Methanotrophs)	SMMO	DNF (Denitrifiers-nirS and nirK)	AOB (ammonia oxidizing bacteria)	PM1 (MTBE aerobic)	RMO (Toluene Monooxygenase)	RDEG (Toluene Monooxygenase)	PHE (Phenol Hydroxylase)	NAH (Napthalene-aerobic)	BSSA (Toluene/Xylene-Anaerobic)	add. qPCR:	add. qPCR:	RNA (Expression Option)*	Other: Geobacter spp GEO	Other:	Other:
002 LI 1	ST012-W30-WG-090314	9/3/14	0900	W												X	X			X											X		
														NOTE: Extra Volume to run additional analyses																		

Relinquished by: [signature] Received by: Judith Hawk Date 9/4/14

It is vital that chain of custody is filled out correctly & that all relative information is provided.
Failure to provide sufficient and/or correct information regarding reporting, invoicing & analyses requested information may result in delays for which MI will not be liable.

* additional cost and sample preservation are associated with RNA samples.

**Saturday delivery: See sampling protocol for alternate shipping address.

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10515 Research Drive
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Client:	Shanda Wagner AMEC E & I, Inc. 4600 East Washington Street Suite 600 Phoenix, AZ 85034	**Phone:**	602-329-0571
		Fax:	

Identifier: 002LI **Date Rec:** 09/03/2014 **Report Date:** 09/09/2014

Client Project #: 9101110001.5300.5301 **Client Project Name:** WAFB-STO12

Purchase Order #: F014200244

Analysis Requested: CENSUS, PLFA

Reviewed By:

MICROBIAL INSIGHTS, INC.

10515 Research Dr., Knoxville, TN 37932
Tel. (865) 573-8188 Fax. (865) 573-8133

CENSUS

Client: AMEC E & I, Inc.
Project: WAFB-STO12

MI Project Number: 002LI
Date Received: 09/03/2014

Sample Information

Client Sample ID:		**STO12-W30-WG-090214**	**STO12-W11-WG-090214**
Sample Date:		09/02/2014	09/02/2014
Units:		cells/mL	cells/mL
Analyst:		RW	RW
Functional Genes			
Denitrifying Bacteria	nirK	**4.89E+05**	**4.52E+05**
Denitrifying Bacteria	nirS	**3.20E+04**	**1.93E+04**
Other Genera			
Geobacter spp.	*GEO*	**1.06E+04**	**1.53E+04**
Phylogenetic Group			
Sulfate Reducing Bacteria	APS	**4.37E+04**	**6.49E+05**
Methanogen	MGN	**6.42E+04**	**7.00E+04**

Legend:
NA = Not Analyzed NS = Not Sampled J = Estimated gene copies below PQL but above LQL I = Inhibited
< = Result not detected

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Client: Shanda Wagner
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Suite 600
Phoenix, AZ 85034

Phone: 602-329-0571

Fax:

Identifier: 002LI **Date Rec:** 09/03/2014 **Report Date:** 09/18/2014

Client Project #: 9101110001.5300.5301 **Client Project Name:** WAFB-STO12

Purchase Order #: F014200244

Analysis Requested: CENSUS, PLFA

Reviewed By:

Kate Clark

MICROBIAL INSIGHTS, INC.

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PLFA

Client:	**AMEC E & I, Inc.**	**MI Project Number:**	**002LI**
Project:	WAFB-STO12	Date Received:	09/03/2014

Sample Information

Sample Name:	**STO12-W30-WG -090214**	**STO12-W11-WG -090214**
Sample Date:	09/02/2014	09/02/2014
Sample Matrix:	Water	Water
Analyst:	BJ	BJ

Biomass

Total Biomass (cells/mL)	**1.02E+04**	**4.39E+04**

Community Structure (% total PLFA)

Firmicutes (TerBrSats)	**24.57**	**20.44**
Proteobacteria (Monos)	**36.93**	**45.98**
Anaerobic metal reducers (BrMonos)	**1.54**	**1.91**
SRB/Actinomycetes (MidBrSats)	**4.13**	**3.21**
General (Nsats)	**32.08**	**27.09**
Eukaryotes (polyenoics)	**0.75**	**1.37**

Physiological Status (Proteobacteria only)

Slowed Growth	**0.75**	**0.78**
Decreased Permeability	**0.00**	**0.16**

Legend:
NA = Not Analyzed NS = Not Sampled

MICROBIAL INSIGHTS, INC.

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PLFA

Client:	**AMEC E & I, Inc.**	**MI Project Number:**	**002LI**
Project:	WAFB-STO12	Date Received:	09/03/2014

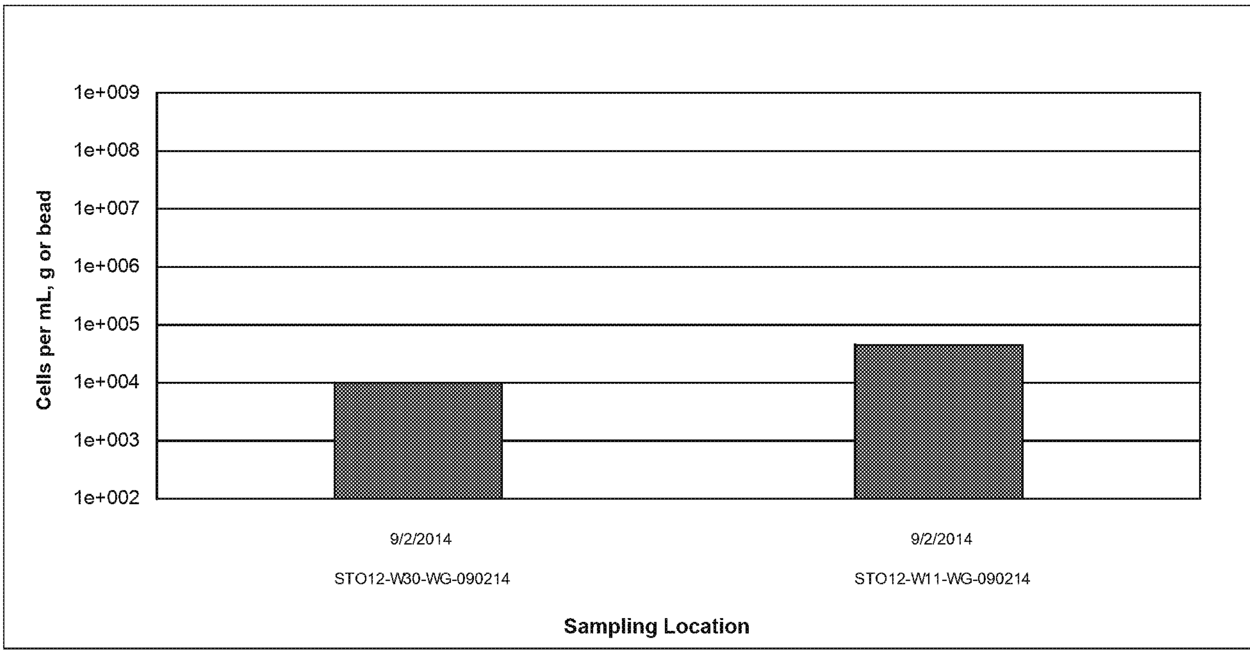

Figure 1. Biomass content is presented as a cell equivalent based on the total amount of phospholipid fatty acids (PLFA) extracted from a given sample. Total biomass is calculated based upon PLFA attributed to bacterial and eukaryotic biomass

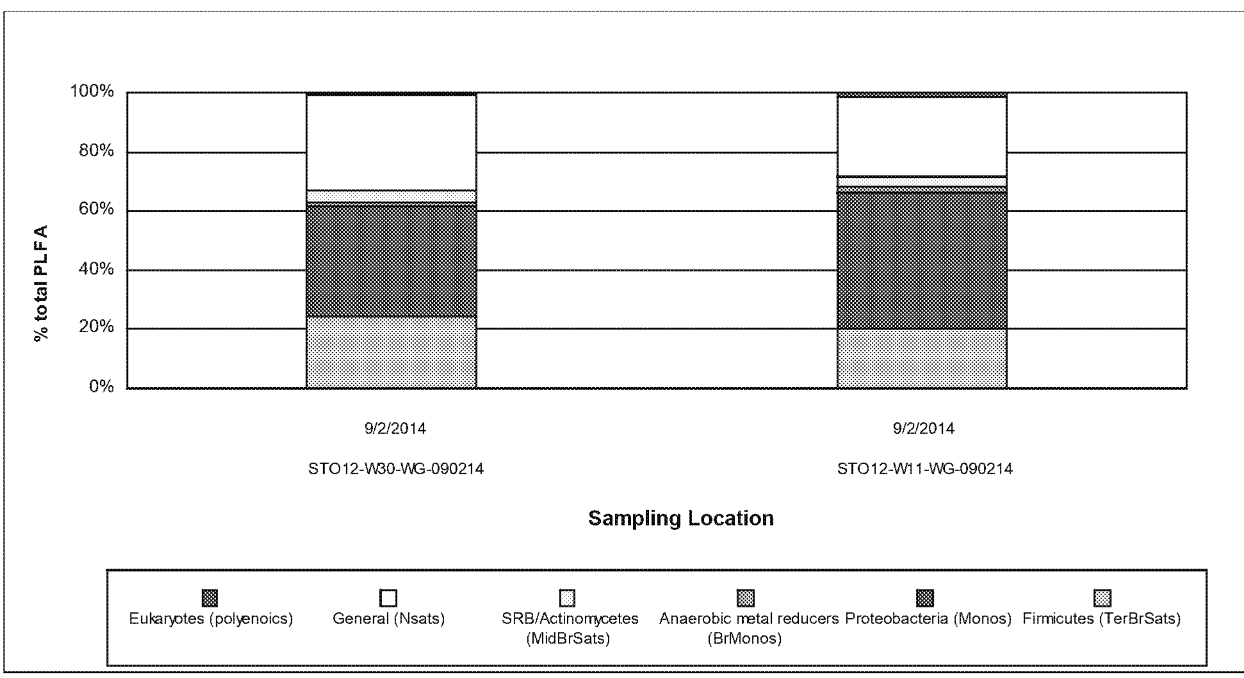

Figure 2. Relative percentages of total PLFA structural groups in the samples analyzed. Structural groups are assigned according to PLFA chemical structure, which is related to fatty acid biosynthesis.

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Client: Stuart Pearson
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Portland, ME 04101

Phone:

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Identifier: 015LI **Date Rec:** 09/09/2014 **Report Date:** 09/17/2014

Client Project #: 9101110001.5300.5301 **Client Project Name:** FWAFB ST012 EBR

Purchase Order #: F014200244

Analysis Requested: CENSUS, PLFA

Reviewed By:

MICROBIAL INSIGHTS, INC.

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CENSUS

Client: **AMEC E & I, Inc.**
Project: FWAFB ST012 EBR

MI Project Number: **015LI**
Date Received: 09/09/2014

Sample Information

Client Sample ID:		**ST012-W11-WG -090814**	**ST012-W30-WG -091014**
Sample Date:		09/08/2014	09/10/2014
Units:		cells/mL	cells/mL
Analyst:		RW	RW
Functional Genes			
Denitrifying Bacteria	nirK	**5.93E+05**	**3.87E+05**
Denitrifying Bacteria	nirS	**4.87E+04**	**1.16E+04**
Other Genera			
Geobacter spp.	*GEO*	**7.88E+02**	**1.17E+05**
Phylogenetic Group			
Sulfate Reducing Bacteria	APS	**2.76E+06**	**2.00E+05**
Methanogen	MGN	**4.41E+03**	**4.68E+04**

Legend:
NA = Not Analyzed NS = Not Sampled J = Estimated gene copies below PQL but above LQL I = Inhibited
< = Result not detected

microbial insights

10515 Research Drive
Knoxville, TN 37932
Phone: (865) 573-8188
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Client: Stuart Pearson
AMEC E & I, Inc.
511 Congress Street
Portland, ME 04101

Phone:

Fax:

Identifier: 015LI **Date Rec:** 09/09/2014 **Report Date:** 09/26/2014

Client Project #: 9101110001.5300.5301 **Client Project Name:** FWAFB ST012 EBR

Purchase Order #: F014200244

Analysis Requested: CENSUS, PLFA

Reviewed By:

Kate Clark

MICROBIAL INSIGHTS, INC.

10515 Research Dr., Knoxville, TN 37932
Tel. (865) 573-8188 Fax. (865) 573-8133

PLFA

Client:	**AMEC E & I, Inc.**	**MI Project Number:**	**015LI**
Project:	FWAFB ST012 EBR	Date Received:	09/09/2014

Sample Information

Sample Name:	**ST012-W11-WG -090814**	**ST012-W30-WG-091014**
Sample Date:	09/08/2014	09/10/2014
Sample Matrix:	Water	Water
Analyst:	BJ	BJ

Biomass

Total Biomass (cells/mL)	**4.60E+04**	**4.15E+04**

Community Structure (% total PLFA)

Firmicutes (TerBrSats)	**0.52**	**14.07**
Proteobacteria (Monos)	**76.03**	**50.65**
Anaerobic metal reducers (BrMonos)	**0.00**	**1.55**
SRB/Actinomycetes (MidBrSats)	**0.48**	**0.90**
General (Nsats)	**22.42**	**30.95**
Eukaryotes (polyenoics)	**0.55**	**1.89**

Physiological Status (Proteobacteria only)

Slowed Growth	**0.05**	**0.25**
Decreased Permeability	**0.00**	**0.07**

Legend:
NA = Not Analyzed NS = Not Sampled

MICROBIAL INSIGHTS, INC.

10515 Research Dr., Knoxville, TN 37932
Tel. (865) 573-8188 Fax. (865) 573-8133

PLFA

Client:	**AMEC E & I, Inc.**	**MI Project Number:**	**015LI**
Project:	FWAFB ST012 EBR	Date Received:	09/09/2014

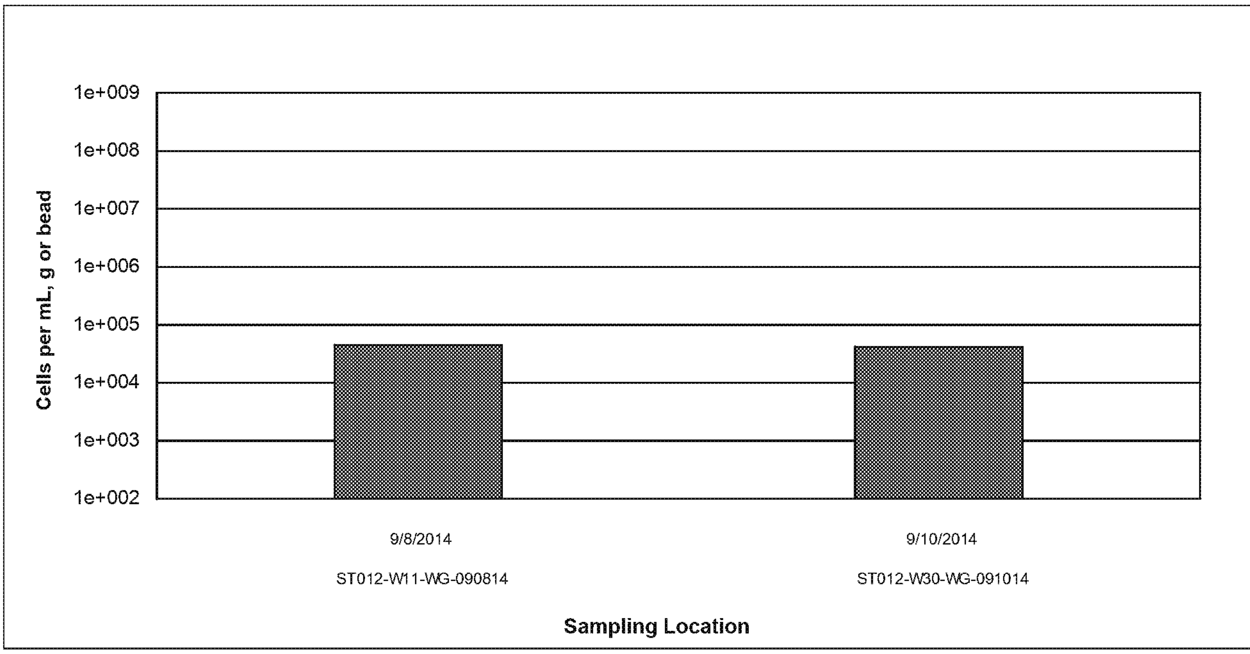


Figure 1. Biomass content is presented as a cell equivalent based on the total amount of phospholipid fatty acids (PLFA) extracted from a given sample. Total biomass is calculated based upon PLFA attributed to bacterial and eukaryotic biomass

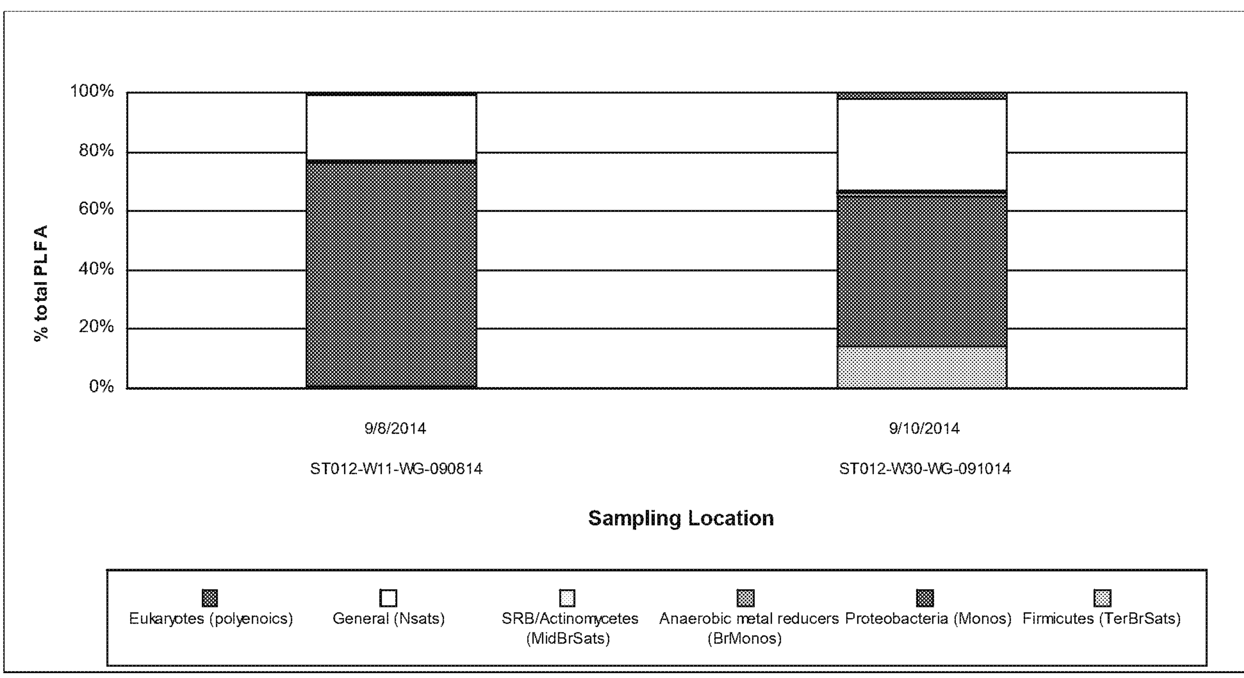


Figure 2. Relative percentages of total PLFA structural groups in the samples analyzed. Structural groups are assigned according to PLFA chemical structure, which is related to fatty acid biosynthesis.

APPENDIX E

MICROBIAL KINETICS ESTIMATION

Job No.	9101110001	Sheet	1	of	1	
Phase		Task				
Job Name	Former Williams AFB Site ST012					
By	S. Beadle	Date	2015-04-17			
Checked By	S. Pearson	Date	2015-05-6			511 Congress Street
Updated by		Date				Portland, ME 04101
Checked By		Date				+1 (207) 775-5401

Purpose: To calculate the Michaelis-Menten kinetic parameters: the Michaelis-Menten coefficient - the substrate (sulfate) concentration when the reaction rate is at half its maximum (K_M), and the maximum substrate utilization rate (v_{max}) to estimate sulfate utlization due to microbial activity in wells W11 and W30 during the shut-in period of each well's push-pull test. These parameters can then be used to estimate the degradation rate constant for the site.

Methods: Using the Lineweaver-Burk method, the reciprocal of the Michaelis-Menten (M-M) kinetic equation is plotted and the linear relationship between the inverse of the sulfate utilization rate and the inverse of the sulfate concentration can be used to estimate v_{max} and K_M, as shown below:

Michaelis-Menten Kinetic Equation:

$$v = \frac{(V_{max}[S])}{(K_M + [S])}$$

Reciprocal:

$$\frac{1}{v} = \left(\frac{K_M}{v_{max}}\right)\left(\frac{1}{[S]}\right) + \left(\frac{1}{v_{max}}\right)$$

Where:
v= sulfate utilization rate [g/day]
K_M= Michaelis-Menten coefficient [mg/l]
v_{max}= maximum sulfate utlization rate [g/day]
[S]= sulfate concentration [g/L]

(1/v) is plotted on the y-axis and (1/[S]) is plotted on the x-axis. Linear regression can then be used to estimate the y-intercept ($1/v_{max}$) and the slope (K_M/v_{max}) of the graph

Given the daily analytical data for both bromide and sulfate concentrations during the shut-in period of the test, 1/[S] and 1/v can be calculated to plot the reciprocal M-M equation to perform the Lineweaver-Burk method for both W11 and W30.

Once K_M and V_{max} have been estimated based on the field test data, they can be used as constants in the Monod kinetic equation to model the exponential decay of TPH.

Monod Kinetic Equation:

$$v = v_{max}\left(\frac{[S]}{K_M + [S]}\right)$$

Because the sulfate (and total petroleum hydrocarbon [TPH]) utilization rate is time-dependent, the M-M kinetic parameters are entered into the Monod kinetic equation to model the sulfate utlization rate as a step function of time for each day after degradation begins. The utilization rate for each day can then be used to estimate the TPH concentration for each step. The plot of the TPH concentration versus time since the the start of degradation can be expressed as first-order exponential decay:

$$[TPH] = [TPH_o]e^{-kt}$$

Where:
[TPH]= TPH Concentration mg/l
$[TPH_o]$= Initial TPH Concentration mg/l
k= degradation rate constant day^{-1}

The exponential decay model assumes that TPH (the substrate) is not rate-limiting, therefore this input is much larger than concentrations typically found during groundwater sampling at the site.

An exponential fit can be applied to the modeled TPH decay to estimate the degradation rate constant (k) for TPH.

Assumptions:

1. Microbial sulfate utilization in groundwater abides by Michaelis-Menten and Monod kinetics. This assumption includes that the substrate is not rate limiting - that there is more available substrate than K_M.
2. TPH degradation was a first-order reaction for the duration of the field test.
3. The stoichiometric relationship between sulfate and TPH: 5.25 Sulfate to 1 TPH

Constants and Inputs:

Summary of Shut-in Period Sulfate and Bromide Concentrations

		ST012–W11		ST012–W30	
Sample Type	**Date**	**Bromide [mg/l]**	**Sulfate [mg/l]**	**Bromide [mg/l]**	**Sulfate [mg/l]**
Baseline	7/16/2012	1.6	5.4	1.3	11
Shut-in	7/22/2014	55	1000	99	1900
Shut-in	7/24/2014	39	2000	92	1600
Shut-in	7/29/2014	18	940	47	840
Shut-in	7/31/2014	12	610	35	660
Shut-in	8/5/2014	6.2	300	20	320
Shut-in	8/7/2014	4.9	230	16	240
Shut-in	8/12/2014	3	110	11	140
Shut-in	8/15/2014	2.4	73	8.7	100
Shut-in	8/19/2014	1.9	42	6.5	67
Shut-in	8/21/2014	1.8	31	5.2	49
Shut-in	8/26/2014	1.6	18	4.5	34
Shut-in	8/29/2014	1.5	14	3.9	24
Post-Shut-In	9/2/2014	2.6	6.4	3.5	18
Injected Solution		151	4294	151	4294

NOTES:
mg/l – milligrams per liter.

Total mass of sulfate injected from potassium sulfate solution 6615 grams
Initial bromide solution volume 1514 L

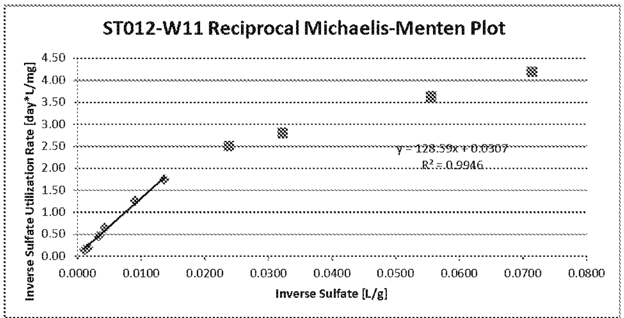
Job No.	9101110001	Sheet	1 of 1	
Phase		Task		
Job Name	Former Williams AFB Site ST012			
By	S. Beadle	Date	2015-04-17	
Checked By	S. Pearson	Date	2015-05-6	511 Congress Street
Updated by		Date		Portland, ME 04101
Checked By		Date		+1 (207) 775-5401

Calculations:

ST012-W11										
Date	Normalized Bromide Concentration [-]	Normalized Sulfate Concentration [-]	Change in Normalized Bromide Concentration[1] [-]	Change in Normalized Sulfate Concentration[1] [-]	Cumulative Sulfate Respired [g]	Average Sulfate Utilization Rate Since Start [g/day]	Volume of Water in Reaction (L)	Average Sulfate Utilization Rate Since Start [mg/l*day]	Inverse Sulfate Conc. [l/mg]	Inverse Sulfate Utilization Rate [l*day/mg]
7/21/2014										
7/22/2014	0.364	0.233					4,200			
7/24/2014	0.258	0.466	0.106	-0.233	-2241		5,900			
7/29/2014	0.119	0.219	0.139	0.247	715	89.3	12,700	7.033	0.0011	0.14
7/31/2014	0.0794	0.142	0.040	0.077	960	96.0	19,100	5.029	0.0016	0.20
8/5/2014	0.0410	0.070	0.038	0.072	1184	79.0	36,900	2.140	0.0033	0.47
8/7/2014	0.0324	0.054	0.009	0.016	1235	72.7	46,700	1.556	0.0043	0.64
8/12/2014	0.0198	0.026	0.013	0.028	1337	60.8	76,300	0.797	0.0091	1.26
8/15/2014	0.0159	0.017	0.004	0.009	1368	54.7	95,400	0.574	0.0137	1.74
8/19/2014	0.0126	0.010	0.003	0.007	1394	48.1	120,500	0.399	0.0238	2.51
8/21/2014	0.0119	0.007	0.001	0.003	1406	45.4	127,200	0.357	0.0323	2.80
8/26/2014	0.0106	0.004	0.001	0.003	1418	39.4	143,100	0.275	0.0556	3.63
8/29/2014	0.0099	0.003	0.001	0.001	1419	36.4	152,600	0.239	0.0714	4.19
9/2/2014	0.0172	0.001	-0.007	0.002	1479	34.4	88,100	0.390	0.1563	2.56

Note:

[1] Because initial data indicated greater bromide reduction than sulfate, the grams of sulfate respired was estimated using the change in normalized bromide and sulfate concentrations rather than caluclating the cumulative grams as done for W30 below.



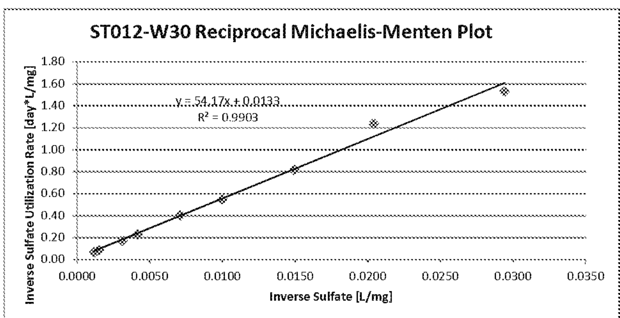
ST012-W11 Reciprocal Michaelis-Menten Plot

y=mx+b

m=	128.587 day
b=	0.0307 L*day/mg
v_{max}=	32.57 mg/l*day
K_M=	4188.3 mg/l

Note: Initial readings were used to estimate parameters due to shift in slope above inverse sulfate of 0.02.

Date	ST012-W30								
	Normalized Bromide Concentration [-]	Normalized Sulfate Concentration [-]	Cumulative Grams	Cumulative Sulfate Respired [g]	Average Sulfate Utilization Rate Since Start [g/day]	Volume of Water in Reaction [L]	Average Sulfate Utilization Rate Since Start [mg/l*day]	Inverse Sulfate Conc. [L/mg]	Inverse Sulfate Utilization Rate [L*day/mg]
7/18/2014									
7/22/2014	0.655	0.443	1403			2313			
7/24/2014	0.608	0.373	1559	-156		2489			
7/29/2014	0.311	0.196	762	798	72.5	4871	14.884	0.0012	0.07
7/31/2014	0.231	0.154	514	1045	80.4	6542	12.289	0.0015	0.08
8/5/2014	0.132	0.075	382	1177	65.4	11448	5.714	0.0031	0.18
8/7/2014	0.106	0.056	330	1229	61.5	14310	4.295	0.0042	0.23
8/12/2014	0.073	0.033	265	1294	51.8	20814	2.486	0.0071	0.40
8/15/2014	0.058	0.023	226	1333	47.6	26317	1.809	0.0100	0.55
8/19/2014	0.043	0.016	181	1378	43.1	35224	1.223	0.0149	0.82
8/26/2014	0.034	0.008	175	1384	35.5	44030	0.806	0.0204	1.24
8/29/2014	0.030	0.006	160	1399	33.3	50879	0.655	0.0294	1.53
9/2/2014	0.026	0.004	143	1416	30.8	58707	0.524	0.0417	1.91



ST012-W30 Reciprocal Michaelis-Menten Plot

y=mx+b

m=	54.17 /day
b=	0.013294152 L*day/mg
v_{max}=	75.22 mg/l*day
K_M=	4075 mg/l

Job No.	9101110001	Sheet	1	of	1
Phase		Task			
Job Name	Former Williams AFB Site ST012				
By	S. Beadle	Date	2015-04-17		
Checked By	S. Pearson	Date	2015-05-6		
Updated by		Date			
Checked By		Date			

511 Congress Street
Portland, ME 04101
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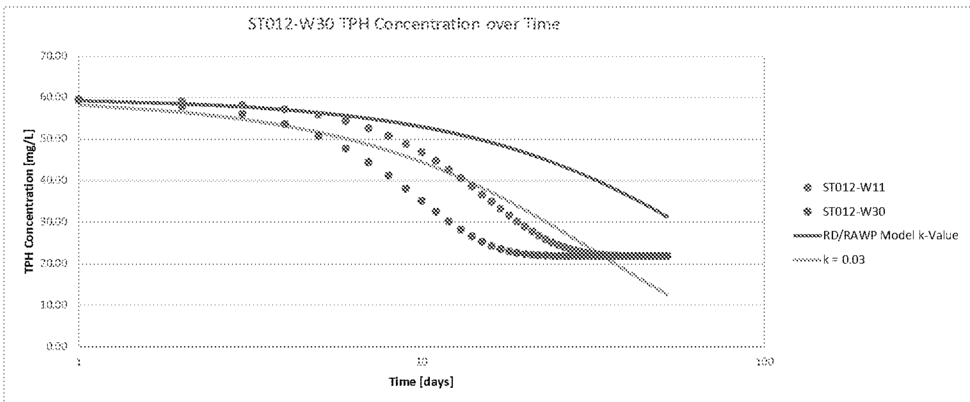
INITIAL CONDITIONS

	W11	W30
Sulfate Concentration	200 mg/l	200 mg/l
Hydrocarbon Concentration	60 mg/l	60 mg/l

RD/RAWP modeling k-value 0.0125 day^{-1}
Best-fit k-value 0.03 day^{-1}

Time	W11			W30			RD/RAWP Model K-Value [k = 0.0125 d^{-1}]	k = 0.03
	[SO4]	Sulfate Utilization Rate	TPH Concentration	Sulfate Concentration	Sulfate Utilization Rate	TPH Concentration		
[day]	[mg/l]	[mg/l/day]	[mg/l]	[mg/l]	[mg/l/day]	[mg/l]		
0	200	1.48	60	200	3.52	60	60	60
1	198.52	1.47	59.72	196.48	3.46	59.33	59.25	58.23
2	195.57	1.45	59.16	189.56	3.34	58.01	58.52	56.51
3	191.21	1.42	58.33	179.53	3.17	56.10	57.79	54.84
4	185.52	1.38	57.24	166.83	2.96	53.68	57.07	53.22
5	178.61	1.33	55.93	152.04	2.71	50.86	56.36	51.64
6	170.62	1.27	54.40	135.80	2.43	47.77	55.66	50.12
7	161.69	1.21	52.70	118.82	2.13	44.54	54.97	48.64
8	152.01	1.14	50.86	101.77	1.83	41.29	54.29	47.20
9	141.74	1.07	48.90	85.27	1.54	38.15	53.62	45.80
10	131.08	0.99	46.87	69.85	1.27	35.21	52.95	44.45
11	120.21	0.91	44.80	55.91	1.02	32.55	52.29	43.14
12	109.30	0.83	42.72	43.69	0.80	30.23	51.64	41.86
13	98.53	0.75	40.67	33.32	0.61	28.25	51.00	40.62
14	88.05	0.67	38.68	24.78	0.45	26.62	50.37	39.42
15	77.99	0.60	36.76	17.96	0.33	25.33	49.74	38.26
16	68.46	0.52	34.95	12.68	0.23	24.32	49.12	37.13
17	59.56	0.46	33.25	8.71	0.16	23.56	48.51	36.03
18	51.34	0.39	31.68	5.82	0.11	23.01	47.91	34.96
19	43.84	0.34	30.26	3.78	0.07	22.63	47.32	33.93
20	37.10	0.29	28.97	2.39	0.04	22.36	46.73	32.93
21	31.09	0.24	27.83	1.46	0.03	22.18	46.15	31.96
22	25.81	0.20	26.82	0.87	0.02	22.07	45.57	31.01
23	21.22	0.16	25.95	0.50	0.01	22.00	45.01	30.09
24	17.28	0.13	25.20	0.28	0.01	21.96	44.45	29.21
25	13.93	0.11	24.56	0.15	0.00	21.93	43.90	28.34
26	11.13	0.09	24.02	0.08	0.00	21.92	43.35	27.50
27	8.80	0.07	23.58	0.04	0.00	21.91	42.81	26.69
28	6.89	0.05	23.22	0.02	0.00	21.91	42.28	25.90
29	5.33	0.04	22.92	0.01	0.00	21.91	41.76	25.14
30	4.09	0.03	22.68	0.00	0.00	21.91	41.24	24.39
31	3.11	0.02	22.50	0.00	0.00	21.91	40.73	23.67
32	2.33	0.02	22.35	0.00	0.00	21.90	40.22	22.97
33	1.74	0.01	22.24	0.00	0.00	21.90	39.72	22.29
34	1.28	0.01	22.15	0.00	0.00	21.90	39.23	21.64
35	0.93	0.01	22.08	0.00	0.00	21.90	38.74	21.00
36	0.67	0.01	22.03	0.00	0.00	21.90	38.26	20.38
37	0.48	0.00	22.00	0.00	0.00	21.90	37.78	19.77
38	0.34	0.00	21.97	0.00	0.00	21.90	37.31	19.19
39	0.23	0.00	21.95	0.00	0.00	21.90	36.85	18.62
40	0.16	0.00	21.94	0.00	0.00	21.90	36.39	18.07
41	0.11	0.00	21.93	0.00	0.00	21.90	35.94	17.54
42	0.07	0.00	21.92	0.00	0.00	21.90	35.49	17.02
43	0.05	0.00	21.91	0.00	0.00	21.90	35.05	16.52
44	0.03	0.00	21.91	0.00	0.00	21.90	34.62	16.03
45	0.02	0.00	21.91	0.00	0.00	21.90	34.19	15.55
46	0.01	0.00	21.91	0.00	0.00	21.90	33.76	15.09
47	0.01	0.00	21.91	0.00	0.00	21.90	33.34	14.65
48	0.01	0.00	21.91	0.00	0.00	21.90	32.93	14.22
49	0.00	0.00	21.91	0.00	0.00	21.90	32.52	13.80
50	0.00	0.00	21.91	0.00	0.00	21.90	32.12	13.39
51	0.00	0.00	21.90	0.00	0.00	21.90	31.72	12.99
52	0.00	0.00	21.90	0.00	0.00	21.90	31.32	12.61



Conclusions: These kinetic values were then used to model the sulfate consumption and TPH degradation using monod-type kinetics and a first-order degradation curve was fitted to these modeled values with an emphasis on fitting the early part of the degradation curve. The graphically approximated first-order maximum TPH degradation rate coefficient is 0.03 day^{-1}. When compared to a value of 0.0125 day^{-1} for the maximum utilization rate of hydrocarbons other than benzene in the RD/RAWP modeling, the maximum degradation rate under sulfate reducing conditions in the EBR field test was approximately 2.4 times greater than previously modeled. This indicates that the values used in the RD/RAWP may be conservative and are prepresentative of degradation kinetics associated with typical background sulfate flus into the site. The Vmax and Km values indicate the higher degradation rates are possible with higher sulfate concentrations.

APPENDIX D

TESTAMERICA ANALYTICAL REPORTS
(INCLUDED ON CD ONLY)

APPENDIX E

GROUNDWATER MODEL OUTPUTS

Job No.	9101110001	Sheet	1 of 2		
Phase	5200	Task	01		
Job Name	Williams AFB, Site ST012				
By	JDA	Date	10/1/15		
Checked By	SCP	Date	10/2/2015	511 Congress Street	
Revision 1		Date		Portland, ME 04101	
Checked By		Date		+1 (207) 775-5401 Fax +1 (207) 772-4762	

Purpose: Estimate design flow rate for groundwater extraction pumps based on groundwater 3D model results.

Method: Calculate the estimated design flow rate for groundwater extraction pumps based on 3D groundwater model results using proposed stress periods.

Assumptions:

1. Subsurface geology developed based on previous boring logs.
2. Model assumes ideal operations with no downtime.
3. Pumps are controlled based on drawdown and not constant flow rate.

Constants and Inputs: Stress period table for 3D groundwater transient model:

STRESS PERIOD	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
DURATION (days)	75	6	39	50	10	20	20	20	20	20	10	10	30	85	115	20	30	1440
TOTAL TIME (days)	75	81	120	170	180	200	220	240	260	280	290	300	330	415	530	550	580	2020
ST012-CZ18	X																	
ST012-UWBZ31-EBR	X																	
ST012-CZ21-EBR	X	X																
ST012-CZ19		X	X															
ST012-LSZ39	X	X	X	X														
ST012-UWBZ26	X	X	X	X	X													
ST012-LSZ11	X	X	X	X	X	X												
ST012-LSZ37	X	X	X	X	X	X	X											
ST012-LSZ38	X	X	X	X	X	X	X	X										
ST012-LSZ23	X	X	X	X	X	X	X	X	X									
ST012-UWBZ27	X	X	X	X	X	X	X	X	X									
ST012-LSZ29	X	X	X	X	X	X	X	X	X	X								
ST012-LSZ36	X	X	X	X	X	X	X	X	X	X	X							
ST012-LSZ14	X	X	X	X	X	X	X	X	X	X	X	X						
ST012-UWBZ22	X	X	X	X	X	X	X	X	X	X	X	X	X					
ST012-LSZ12	X	X	X	X	X	X	X	X	X	X	X	X	X	X				
ST012-UWBZ10	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X			
ST012-UWBZ30-EBR	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		
ST012-LSZ26	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	

NOTES:
X- Pump on well is on, otherwise off
No pumping during stress period 18. Ambient flow for 1440 days

Water level elevation set points for each screened interval:

Well	Drawdown Setpoint (ft bgs)
ST012-CZ18	155
ST012-CZ19	155
ST012-CZ21-EBR	155
ST012-LSZ11	180
ST012-LSZ12	195
ST012-LSZ14	180
ST012-LSZ23	180
ST012-LSZ26	195
ST012-LSZ29	180
ST012-LSZ36	180
ST012-LSZ37	180
ST012-LSZ38	180
ST012-LSZ39	180
ST012-UWBZ10	155
ST012-UWBZ22	155
ST012-UWBZ26	155
ST012-UWBZ27	155
ST012-UWBZ30-EBR	155
ST012-UWBZ31-EBR	155

References:

AMEC, 2014. Final Remedial Design and Remedial Action Work Plan, Operable Unit 2, Site ST012, Former Williams Air Force Base, Mesa, Arizona. April 10, 2014.

Job No.	9101110001	Sheet	2 of 2		
Phase	5200	Task	01		
Job Name	Williams AFB, Site ST012				
By	JDA	Date	10/1/15		
Checked By	SCP	Date		511 Congress Street	
Revision 1		Date		Portland, ME 04101	
Checked By		Date		+1 (207) 775-5401 Fax +1 (207) 772-4762	

Calculations: Design flow rate table developed from 3D groundwater model output.

Well	Flow Rate (GPM)
CZ18	11.07
CZ19	7.49
CZ21	6.88
UWBZ10	4.02
UWBZ22	1.88
UWBZ26	1.58
UWBZ27	0.87
UWBZ30	0.79
UWBZ31	2.34
LSZ09	1.56
LSZ11	1.45
LSZ12	3.88
LSZ14	0.01
LSZ17	6.31
LSZ23	1.65
LSZ26	2.28
LSZ28	6.37
LSZ29	9.36
LSZ36	2.43
LSZ37	1.89
LSZ38	2.02
LSZ39	1.54
Total Extraction Flow Rate:	77.67
Averag Extraction Flow Rate per Well:	3.53

Conclusion: Predicted flow rates for each of the 22 proposed groundwater extraction wells were developed using the existing 3D groundwater model. The total expected design flow rate is expected to be approximately 77 gallons per minute (gpm), with an average individual well flow rate of about 3.5 gpm. Actual flow rates at each well are expected to vary from the predicted flow rates; however, the average flow per well is expected to be similar to that predicted by the model.

Legend

- CZ, Injection
- CZ, Extraction
- CZ Pathlines
- CZ LNAPL Extent

Notes: CZ - Cobble Zone
LNAPL - Light Non-Aqueous Phase Liquid

Time arrows are at 90 day increments.

0 100 200 Feet

N

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Remedial Design/Remedial Action Work Plan
Former Williams Air Force Base
Mesa, Arizona

MODELED TEA INJECTION PATHLINES
COBBLE ZONE
160 FT BGS

FIGURE
E-1

Job No.	9101110001
PM:	EW
Date:	9/30/2015
Scale:	1" = 100 feet

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P:_Modeling-Working\WAFB\ST012_EBR_TSwGHB_093015\GIS\WAFB_ST012_EBR_093015results_cz.mxd 10/1/2015 11:57:00 AM jodi.clark

Legend

- UWBZ, Injection
- UWBZ, Extraction
- UWBZ Pathlines
- UWBZ LNAPL Extent

Notes: UWBZ - Upper Water Bearing Zone
LNAPL - Light Non-Aqueous Phase Liquid

Time arrows are at 90 day increments.

0 100 200 Feet

N

Draft, Addendum #2
Remedial Design/Remedial Action Work Plan
Former Williams Air Force Base
Mesa, Arizona

MODELED TEA INJECTION PATHLINES
UPPER WATER BEARING ZONE
180 FT BGS

FIGURE **E-2**

Job No.	9101110001
PM:	EW
Date:	9/30/2015
Scale:	1" = 100 feet

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Legend

- LSZ, Injection
- LSZ, Extraction
- LSZ Pathlines
- LSZ LNAPL Extent

Notes: LSZ - Lower Saturated Zone
LNAPL - Light Non-Aqueous Phase Liquid

Time arrows are at 90 day increments.

0 100 200 Feet

N

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Remedial Design/Remedial Action Work Plan
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Mesa, Arizona

MODELED TEA INJECTION PATHLINES LOWER SATURATED ZONE 220 FT BGS

FIGURE E-3

Job No.	9101110001
PM:	EW
Date:	9/30/2015
Scale:	1" = 100 feet

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APPENDIX F

TEA INJECTION WELL DISTRIBUTION CALCULATIONS

Job No.	9101110001	Sheet	1 of 3		
Phase	5200	Task	01		
Job Name	Williams AFB, Site ST012				
By	JDA	Date	9/28/2015		
Checked By	SCP	Date	10/1/2015		
Revision 1		Date			
Checked By		Date			

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Purpose: To determine the amount of terminal electron acceptor required for each injection well.

Method:
1 - Estimate the area of influence for each individual well (in square feet).
2 - Estimate percentage of total TEA per well based on area of influence of each individual well and estimated SEE treatment
3 - Estimate terminal electron accepter per well based on percentage of total TEA.

Assumptions:
a. Groundwater flow at the site is predominantly from west to east.
b. BTEX+N concentration is constant within modeled extents.
c. Pre-EBR mass and estimated overall sodium sulfate per calculations in Appendix A of RD/RAWP addendum

Constants and Inputs:
SEE mass removals (applied to reduce area influence in the different zones [TTZ, TIZ, ROI, Untreated)

	TTZ	TIZ	ROI
% Reduction	90%	60%	30%

39 tons	Calculated mass of TEA required to reach remedial goals in the CZ
1702 tons	Calculated mass of TEA required to reach remedial goals in the UWBZ
2033 tons	Calculated mass of TEA required to reach remedial goals in the LPZ
684.5 tons	Calculated mass of TEA required to reach remedial goals in the LSZ
30%	Assumed Fraction Required to treat BTEX+N

References: AMEC Foster Wheeler 2015. Mass estimate calculations, Appendix A of RD/RAWP Addendum #2.

Calculations: **1 - Estimate the area of influence for each individual well (in square feet).**

Injection Well	Total Area of Drawn Polygon	Area of Remaining BTEX+N (sq ft) TTZ	TIZ	ROI	Untreated	Total Area Check
CZ						
ST012-CZ22-EBR	18594	4112	5983	6969	1530	18594
ST012-CZ12-MPE	3041	0	240	805	1996	3041
ST012-CZ14-MPE	7973	1134	2807	2383	1649	7973
ST012-CZ16-MPE	1797	0	0	33	1764	1797
UWBZ						
ST012-UWBZ28-EBR	32109	27764	4178	167	0	32109
ST012-UWBZ29-EBR	14727	9484	3793	1450	0	14727
ST012-UWBZ21-MPE	6474	446	1603	3098	1327	6474
ST012-UWBZ23-MPE	8722	1201	2876	3003	1642	8722
ST012-UWBZ32-EBR	8661	890	4693	3078	0	8661
ST012-UWBZ33-EBR	19281	13514	3748	2019	0	19281
ST012-UWBZ34-EBR	24664	14028	3326	3304	4006	24664
ST012-UWBZ35-EBR	6480	1953	1294	1456	1777	6480
ST012-UWBZ36-EBR	27739	18148	3214	2287	4090	27739
LSZ						
ST012-W30	15168	8919	1570	1022	3657	15168
ST012-LSZ51-EBR	9916	9083	833	0	0	
ST012-LSZ50-EBR	37629	33160	2306	1426	737	37629
ST012-LSZ49-EBR	46319	46050	269	0	0	46319
ST012-W11	12025	8441	1540	1210	834	12025
ST012-LSZ48-EBR	8288	7411	877	0	0	8288
ST012-LSZ47-EBR	4799	4558	241	0	0	4799
ST012-LSZ46-EBR	1242	1189	53	0	0	1242
ST012-W37	523	523	0	0	0	523
ST012-LSZ45-EBR	4185	4185	0	0	0	4185
ST012-W34	1023	1023	0	0	0	1023
ST012-LSZ44-EBR	2571	2381	190	0	0	2571
ST012-W36	5571	5089	482	0	0	5571
ST012-LSZ43-EBR	33439	32106	1333	0	0	33439

Job No.	9101110001	Sheet	2 of 3		
Phase	5200	Task	01		
Job Name	Williams AFB, Site ST012				
By	JDA	Date	9/28/2015		
Checked By	SCP	Date	10/1/2015		
Revision 1		Date			
Checked By		Date			

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2 - Estimate percentage of total TEA per well based on area of influence of each individual well and estimated SEE treatment.

Because the mass distribution of BTEX+N is assumed constant across the modeled extents, multiply the square footage of the area by the percent removal to determine remaining BTEX+N by area.

Injection Well	Adjusted for SEE Treatment (sq ft)				
	TTZ	TIZ	ROI	Untreated	Total
CZ					
ST012-CZ22-EBR	411	2393	4878	1530	9213
ST012-CZ12-MPE	0	96	564	1996	2656
ST012-CZ14-MPE	113	1123	1668	1649	4553
ST012-CZ16-MPE	0	0	23	1764	1787
UWBZ					
ST012-UWBZ28-EBR	2776	1671	117	0	4565
ST012-UWBZ29-EBR	948	1517	1015	0	3481
ST012-UWBZ21-MPE	45	641	2169	1327	4181
ST012-UWBZ23-MPE	120	1150	2102	1642	5015
ST012-UWBZ32-EBR	89	1877	2155	0	4121
ST012-UWBZ33-EBR	1351	1499	1413	0	4264
ST012-UWBZ34-EBR	1403	1330	2313	4006	9052
ST012-UWBZ35-EBR	195	518	1019	1777	3509
ST012-UWBZ36-EBR	1815	1286	1601	4090	8791
LSZ					
ST012-W30	892	628	715	3657	5892
ST012-LSZ51-EBR	908	333	0	0	1242
ST012-LSZ50-EBR	3316	922	998	737	5974
ST012-LSZ49-EBR	4605	108	0	0	4713
ST012-W11	844	616	847	834	3141
ST012-LSZ48-EBR	741	351	0	0	1092
ST012-LSZ47-EBR	456	96	0	0	552
ST012-LSZ46-EBR	119	21	0	0	140
ST012-W37	52	0	0	0	52
ST012-LSZ45-EBR	419	0	0	0	419
ST012-W34	102	0	0	0	102
ST012-LSZ44-EBR	238	76	0	0	314
ST012-W36	509	193	0	0	702
ST012-LSZ43-EBR	3211	533	0	0	3744

3 - Estimate mass of TEA required in each zone

Calculated mass of TEA required to reach remedial goals in the CZ	11.66	tons
Calculated mass of TEA required to reach remedial goals in the UWBZ	510.69	tons
Calculated mass of TEA required to reach remedial goals in the LPZ	609.86	tons
Calculated mass of TEA required to reach remedial goals in the LSZ	205.35	tons

Job No.	9101110001	Sheet	3 of 3
Phase	5200	Task	01
Job Name	Williams AFB, Site ST012		
By	JDA	Date	9/28/2015
Checked By	SCP	Date	10/1/2015
Revision 1		Date	
Checked By		Date	

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4 - Estimate terminal electron acceptor per well based on percentage of total TEA.

Determine the percentage of total remaining BTEX+N in each injection well area based on adjusted areas in Step 2. Multiply area percentages by total expected TEA mass.

Injection Well	Calculated Percentage of Zone TEA	Mass of TEA (tons)[1]	Actual Percentage of Zone TEA	Mass of TEA (tons)[2]
CZ				
ST012-CZ22-EBR	50.6%	12	25.0%	12
ST012-CZ12-MPE	14.6%	12	25.0%	12
ST012-CZ14-MPE	25.0%	12	25.0%	12
ST012-CZ16-MPE	9.8%	12	25.0%	12
UWBZ				
ST012-UWBZ28-EBR	9.7%	50	9.7%	79
ST012-UWBZ29-EBR	7.4%	38	7.4%	60
ST012-UWBZ21-MPE	8.9%	45	8.9%	73
ST012-UWBZ23-MPE	10.7%	55	10.7%	87
ST012-UWBZ32-EBR	8.8%	45	8.8%	72
ST012-UWBZ33-EBR	9.1%	46	9.1%	74
ST012-UWBZ34-EBR	19.3%	98	19.3%	157
ST012-UWBZ35-EBR	7.5%	38	7.5%	61
ST012-UWBZ36-EBR	18.7%	96	18.7%	153
LSZ				
ST012-W30	21.0%	43	15.4%	107
ST012-LSZ51-EBR	4.4%	12	4.3%	23
ST012-LSZ50-EBR	21.3%	44	15.6%	109
ST012-LSZ49-EBR	16.8%	34	12.3%	86
ST012-W11	11.2%	23	8.2%	57
ST012-LSZ48-EBR	3.9%	12	4.3%	20
ST012-LSZ47-EBR	2.0%	12	4.3%	12
ST012-LSZ46-EBR	0.5%	12	4.3%	12
ST012-W37	0.2%	12	4.3%	12
ST012-LSZ45-EBR	1.5%	12	4.3%	12
ST012-W34	0.4%	12	4.3%	12
ST012-LSZ44-EBR	1.1%	12	4.3%	12
ST012-W36	2.5%	12	4.3%	13
ST012-LSZ43-EBR	13.3%	27	9.8%	68
Total (all zones)		840		1418

Note

[1] Based on TEA mass in each zone (CZ, UWBZ, and LSZ) estimated in step 3. TEA demand for LPZ not specifically targeted. Minimum 12.1 tons of TEA injected per well.

[2] Based on TEA mass in each zone (CZ, UWBZ, and LSZ) estimated in step 3 with LPZ TEA demand split between UWBZ and LSZ.

CZ - cobble zone
LPZ - low permeability zone
LSZ - lower saturated zone
TEA - terminal electron acceptor
UWBZ - upper water bearing zone

APPENDIX G

AQUIFER ARSENIC LOADING CALCULATIONS

Job No.	9101110001	Sheet	1 o 1	
Phase	5200	Task	01	
Job Name	Williams AFB, Site ST012			
By	JDA	Date	8/27/2015	
Checked By	SCP	Date	10/1/2015	511 Congress Street
Revision 1		Date		Portland, ME 04101
Checked By		Date		+1 (207) 775-5401 Fax +1 (207) 772-4762

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Purpose: To determine the estimated concentration of arsenic in the site aquifer after TEA injection

Method:
1 - Estimate the volume of the aquifer.
2 - Estimate the total mass of arsenic injected during EBR remedial action.
3 - Determine the final concentration of arsenic in the aquifer after injection.

Assumptions:
a. Arsenic will only be injected into saturated pore space represented by the volume of LNAPL modeled on-site. While this is an unlikely reality, this would be the minimum volume of the subsurface for injections representing the most conservative estimate of arsenic concentration post-injection.
b. All sodium sulfate utilized has the same concentration of arsenic.
c. All batches injected have the same concentration of sodium sulfate.
d. Groundwater elevation of 150 ft bgs, leaving 66% of cobble zone in saturated zone.

Constants and Inputs:

0.95	ppm	Minimum As concentration in sodium sulfate, based on Q2 Quality Assurance data provided by Searles Valley Minerals
3	ppm	Maximum As concentration in sodium sulfate, based on maximum arsenic concentration on Searles Valley Minerals sodium sulfate spec sheet
32%	-	Sodium sulfate concentration in injectate solution
1,180	tons	Total mass of sodium sulfate injected during EBR remedial action.

Conversion factors:

453.6	grams per pound
2,000	pounds per ton
3.785	liters per gallon

	Data from Searles Valley Minerals QA
	0.8
	0.7
	1.1
	0.6
	0.9
	1.2
	0.5
	0.9
	0.7
	1
	0.9
	0.9
	1.4
	1.1
	1.1
	0.7
	1.4
	1.2
Avg	0.95

References:
Sodium sulfate specification sheet supplied by Brenntag Chemical on behalf of Searles Valley Minerals.
AMEC Foster Wheeler 2015. Mass estimate calculations as of August 26, 2015, performed by Amec Foster Wheeler, internal draft.

Calculations: **1 - Estimate the volume of the aquifer.**

Volume of the aquifer is assumed to be the volume of pore space in LNAPL volume.

Excerpt from AMEC Foster Wheeler 2015 mass estimate calculations indicating modeled porespace of LNAPL for the base volume:

	LNAPL Volume Interpretation				
	Pore Space Within TTZ (cu ft)	Pore Space between TTZ and TIZ (cu ft)	Pore Space between TIZ and ROI Contour (cu ft)	Pore Space beyond ROI Contour (cu ft)	Total Pore Space (cu ft)
CZ	76,800	19,875	4,725	1,500	102,900
UWBZ	550,350	185,625	133,950	97,125	967,050
LPZ	504,923	81,743	52,493	39,893	679,050
LSZ	1,257,825	92,700	17,400	40,722	1,408,647

Total saturated porespace is summed up with the following equation:

$V_{PS(UWBZ)}+V_{PS(ULPZ+LLPZ)}+V_{PS(LSZ)}+0.66*V_{PS(CZ)}$

3,122,661 cu ft pore space in saturated zone containing LNAPL
23,357,504 gallons pore space in saturated zone
88,408,154 liters of pore space in saturated zone

2 - Estimate the total mass of arsenic injected during EBR remedial action.

Minimum:

0.95 ppm arsenic sodium sulfate
32% concentration of injection solution
320 g/L concentration of injection solution
0.304 ppm As in injectate
1,180 tons of sodium sulfate injected
2,360,000 pounds of sodium sulfate injected
2.2 pounds of arsenic injected (as impurity)
1,017 grams of arsenic injected (as impurity)
1,016,971 milligrams of arsenic injected (as impurity)

0.012 mg/L or ppm of arsenic in the LNAPL porespace

Maximum:

3 ppm arsenic sodium sulfate
32% concentration of injection solution
320 g/L concentration of injection solution
0.96 ppm As in injectate
1,180 tons of sodium sulfate injected
2,360,000 pounds of sodium sulfate injected
7.1 pounds of arsenic injected (as impurity)
3,211 grams of arsenic injected (as impurity)
3,211,488 milligrams of arsenic injected (as impurity)

0.036 mg/L or ppm of arsenic in the LNAPL porespace

Conclusion:	It is expected that, based on the assumptions made in this calculation, the concentration of arsenic in the aquifer post-TEA injection will be near the GWQ standard of 0.010 mg/L published by the Arizona Department of Environmental Quality. However, due to geochemical reactions not accounted for in this calculation, including precipitation of arsenic, chemical reactions with arsenic upon injection in the subsurface, and groundwater recharge, it is likely that the concentration of arsenic will be below the stated standard at the end of EBR operation.

APPENDIX H

QAPP/SAP WORKSHEETS

UFP-QAPP CROSSWALK

Worksheet No.	Required Information	Included in this Work Plan	Crosswalk to Related Information		
			Related Information Provided in the Work Plan	Not Included in this Work Plan	Reasoning
A. Project Management					
Documentation					
1	Title and Approval Page, Table of Contents, Acronyms and Abbreviations, and Executive Summary	✓			The title and approval page are included in the cover of the addendum to the Work Plan.
2	QAPP/SAP Identifying Information	✓			
3	Distribution List			✓	Cover letter accompanying the addendum to the Work Plan provides distribution
4	Project Personnel Sign-Off Sheet	✓			
Project Organization					
5	Project Organizational Chart	✓			
6	Communication Pathways	✓			
7	Personnel Responsibilities and Qualifications Table	✓			
8	Special Personnel Training Requirements Table	✓			
Project Planning/Problem Definition					
9	Project Planning Session Documentation (including Data Needs tables) Project Scoping Session Participants Sheet			✓	

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Worksheet No.	Required Information		Crosswalk to Related Information		
		Included in this Work Plan	Related Information Provided in the Work Plan	Not Included in this Work Plan	Reasoning
10	Problem Definition, Site History, and Background. Site Maps (historical and present)		Section 1.0 of the RD/RAWP and Section 1.0 of Addendum #2 to the RD/RAWP Work Plan specific addendums to SOPs provided in Attachment A	✓	The information is provided at the beginning of the Work Plan/Addendum to introduce the background and objectives
11	Site-Specific Project Quality Objectives	✓			
12	Measurement Performance Criteria	✓			
13	Sources of Secondary Data and Information Secondary Data Criteria and Limitations Table	✓			
14	Summary of Project Tasks		Section 4.0	✓	The information is provided in the Work Plan to highlight the project tasks.
15	Reference Limits and Evaluation Table	✓			
16	Project Schedule/Timeline Table		Figure 7-1	✓	The information is provided in Figure 7-1 of the Addendum.

Worksheet No.	Required Information		Crosswalk to Related Information		
		Included in this Work Plan	Related Information Provided in the Work Plan	Not Included in this Work Plan	Reasoning
B. Measurement Data Acquisition					
Sampling Tasks					
17	Sampling Design and Rationale	✓			
18	Sampling Locations and Methods/SOP Requirements Table Sample Location Map(s)	✓			
19	Analytical Methods/SOP Requirements Table	✓			
20	Field QC Sample Summary Table	✓			
21	Project Sampling SOP References Table Sampling SOPs	✓	Work Plan specific addendums to SOPs provided in Attachment A	✓	Complete SOPs are provided in Attachment A of the program document (AMEC, 2012c).
22	Field Equipment Calibration, Maintenance, Testing, and Inspection Table			✓	Instrument operation and calibration procedures are provided in the appropriate SOPs, which are included in Attachment A of the program document (AMEC, 2012c).
Analytical Tasks					
23	Analytical SOPs Analytical SOP References Table	✓			
24	Analytical Instrument Calibration Table			✓	Analytical instrument calibration procedures are included in Attachment C of the program document (AMEC, 2012c).

ED_005025_00020247-00051

Worksheet No.	Required Information		Crosswalk to Related Information		
		Included in this Work Plan	Related Information Provided in the Work Plan	Not Included in this Work Plan	Reasoning
25	Analytical Instrument and Equipment Maintenance, Testing, and Inspection Table			✓	Test America's QA Program is included in Attachment C of the program document (AMEC, 2012c).
Sample Collection					
26	Sample Handling System, Documentation Collection, Tracking, Archiving, and Disposal Sample Handling Flow Diagram			✓	Procedures for sample handling are provided in SOP No. 15, *Sample Handling*, in Attachment A of the program document (AMEC, 2012c).
27	Sample Custody Requirements, Procedures/SOPs, Sample Container Identification, and Example Chain-of-Custody Form and Seal			✓	The Project Documents and Records Table is provided in the program document (AMEC, 2012a).
QC Samples					
28	QC Samples Table Screening/Confirmatory Analysis Decision Tree			✓	Analytical laboratory QC sample requirements are provided with the analytical laboratory SOPs in Attachment C of the program document (AMEC, 2012a).
Data Management Tasks					
29	Project Documents and Records Table			✓	

Worksheet No.	Required Information		Crosswalk to Related Information		
		Included in this Work Plan	Related Information Provided in the Work Plan	Not Included in this Work Plan	Reasoning
30	Analytical Services Table Analytical and Data Management SOPs	✓	Analytical Services Table as well as Analytical SOPs not included in the program document.		Analytical and Data Management SOPs are included in the Program QAPP (AMEC, 2012a).
C. Assessment Oversight					
31	Planned Project Assessments Table Audit Checklists			✓	The Planned Project Assessments Table is provided in the Program QAPP (AMEC, 2012a).
32	Assessment Findings and Corrective Action Responses Table			✓	Assessment findings and corrective action responses are provided in the program document (AMEC, 2012a).
33	QA Management Reports Table	✓			
D. Data Review					
34	Verification (Step I) Process Table			✓	Program QAPP Worksheet No. 34 directly references Program QAPP Worksheet No. 31, *Planned Project Assessments Table*, (AMEC, 2012c).
35	Validation (Steps IIa and IIb) Process Table			✓	Program QAPP Worksheet No. 35 directly references Program QAPP Worksheet No. 31, *Planned Project Assessments Table* (AMEC, 2012c).

Worksheet No.	Required Information	Crosswalk to Related Information			
		Included in this Work Plan	Related Information Provided in the Work Plan	Not Included in this Work Plan	Reasoning
36	Validation (Steps IIa and IIb) Summary Table			✓	The Analytical Data Validation (Steps IIA and IIB) Summary Table is provided in the Program QAPP (AMEC, 2012c).
37	Usability Assessment			✓	The Usability Assessment is provided in the Program QAPP (AMEC, 2012c).

QAPP WORKSHEET NO. 2 – UFP-QAPP IDENTIFYING INFORMATION

Site Name/Project Name: **Former Williams AFB**
Operable Unit: **Site Wide**
Contractor Name: **Amec Foster Wheeler Environment & Infrastructure (Amec Foster Wheeler)**
Contract Number: **FA8903-09-D-8572**
Contract Title: **PERFORMANCE-BASED REMEDIATION TASK ORDER FORMER WILLIAMS AFB, ARIZONA Contract FA8903-09-D-8572-0002**

1. This Work Plan was prepared in accordance with the requirements of the *Uniform Federal Policy for Quality Assurance Plans (UFP–QAPP)* (IDQTF, 2005); *EPA Guidance on Systematic Planning using the Data Quality Objectives Process*, *EPA QA/G-4* (EPA, 2006a); *EPA Guidance on Systematic Planning using the Data Quality Objectives Process, (QA/R-5)* (EPA, 2006b); and *Department of Defense Quality Systems Manual for Environmental Laboratories, Version 4.2* (DoD, 2010).

2. Identify regulatory program: National Contingency Plan; Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA)

3. Identify approval entity: Site-specific UFP–QAPP documents and appropriate addendums must be approved by AFCEC, ADEQ, and U.S. EPA Region 9.

4. This is a site-specific UFP–QAPP.

5. List dates of scoping sessions that were held:

Scoping Sessions	Date
Weekly Enhanced Bioremediation Design Conference Call	Multiple dates

6. List dates and titles of any QAPP documents written for previous site work that are relevant to the current investigation.

Title	Date
Enhanced Bioremediation Field Test Plan	October 2014
Remedial Design and Remedial Action Work Plan for Operable Unit 2 Revised Groundwater Remedy (AMEC, 2014b)	May 20, 2014
Performance Based Remediation Program QAPP and Standard Operating Procedures (AMEC, 2012)	July 2012
Appendix G, Quality Assurance Project Plan, Final ST012 Phase 1 Thermal Enhanced Extraction Pilot Test Work Plan (Balanced Environmental Management Systems, Inc. [BEM])	November 2007

7. List organizational partners (stakeholders) and connection with lead organization:

Air Force Civil Engineer Center - lead

U. S. Environmental Protection Agency, Region 9 – regulator

Arizona Department of Environmental Quality - regulator

8. Lead organization

Air Force Civil Engineer Center

9. If any required UFP–QAPP elements or required information are not applicable to the project or are provided elsewhere, then note the omitted elements and provide an explanation for their exclusion below:

See QAPP worksheet crosswalk above.

QAPP WORKSHEET NO. 4 – PROJECT PERSONNEL SIGN-OFF SHEET

Name	Organization/Title/Role	Signature/E-mail Receipt	Date Read
Kevin Garrett	Amec Foster Wheeler/QA Lead and Project Chemist		
Don Smallbeck	Amec Foster Wheeler /Project Manager		
Stuart Pearson	Amec Foster Wheeler /RD/RA Lead		
Peter Guerra	Amec Foster Wheeler /Enhanced Bioremediation Lead		
Natalie Chrisman	Amec Foster Wheeler /Investigation Lead		
Michelle Barker	Amec Foster Wheeler /Data Manager		
Douglas Fisher	Amec Foster Wheeler /Field Lead		
Michelle Johnston	TestAmerica/Project Manager		
Catherine Jerrard	AFCEC/Project Manager		

Notes:
AFCEC – Air Force Civil Engineer Center
QA – Quality Assurance
RD/RA - Remedial Design/Remedial Action
TestAmerica – TestAmerica Laboratories, Inc

Modifications to the Approved Work Plan

This Work Plan will be used to implement only the site-specific tasks described herein as a one-time event. Therefore, modifications to this Work Plan are not anticipated once the Work Plan is finalized following review by AFCEC, EPA, and ADEQ. Changes in Standard Operating Procedures (SOPs) or sample analysis procedures finalized in revisions to the Program QAPP will be adopted into this Work Plan. Only the following activities will require a Work Plan modification addendum submittal:

- Changes or additions to sample collection procedures
- Changes or additions to sample analysis procedures
- Changes in data quality objectives (DQOs) and measurement performance criteria (MPC)
- Data assessment and/or reporting
- Need for new or modified SOPs

Changes in procedure will only be implemented after formal approval is received from the Amec Foster Wheeler PM and QA Lead. Verbal approval may be necessary to expedite project execution. Verbal approvals will be documented and submitted for formal approval as soon as possible.

QAPP WORKSHEET NO. 5 – PROJECT ORGANIZATIONAL CHART

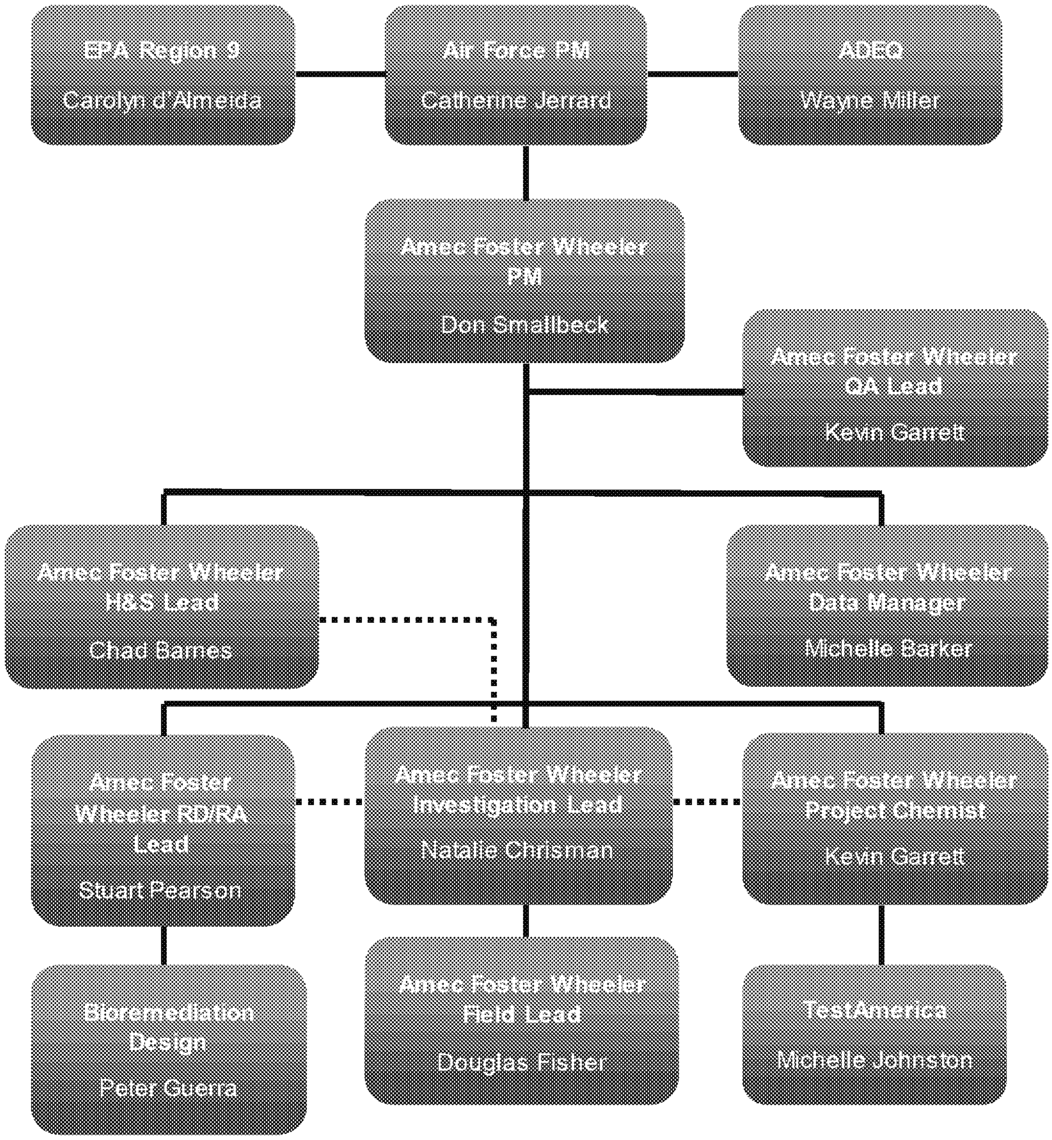
The project organization for investigation and remediation activities, work plan preparation and project execution tasks is provided below. The project will be performed by Amec Foster Wheeler, under contract to AFCEC. Amec Foster Wheeler will manage the project and is completing the work under the CERCLA with regulatory oversight provided by the EPA and the ADEQ. Descriptions of the key project personnel for the AFCEC and Amec Foster Wheeler Teams are provided in Worksheet No. 7.

Amec Foster Wheeler will procure subcontractors to complete specific field activities associated with completing the investigation and remediation activities described in this work plan. These subcontractors include:

- analytical laboratory services
- equipment companies for equipment purchase/rentals (e.g. pumps for sampling)

Analytical services will be provided by TestAmerica Laboratories, Inc. (TestAmerica). In the event that microbial analyses may be necessary, Microbial Insights Inc. (Microbial Insights) will be used. On-site screening data will be used to make internal decisions during field efforts, such as when stabilized readings occur for temperature, pH, specific conductance, etc. before it is appropriate to collect samples for off-site analysis. Field measurements and sampling will be performed by Amec Foster Wheeler employees and these personnel will also perform their activities in accordance with applicable site and task specific work plans and SOPs.

Site-Specific Project Organization Chart



▬▬	Lines of Authority
......	Lines of Communication
ADEQ	Arizona Department of Environmental Quality
EPA	United States Environmental Protection Agency
H&S	Health and Safety
PM	Project Manager
QA	Quality Assurance
RD/RA	Remedial Design/Remedial Action

QAPP WORKSHEET NO. 6 – COMMUNICATIONS PATHWAY

Communication pathways have been defined in detail in the Project Management Plan (AMEC, 2014a) and are reproduced below. These pathways will be used during the ST012 remedial action/site closure activities among the AFCEC, Amec Foster Wheeler, other subcontractors, regulators, and other stakeholders. Amec Foster Wheeler will provide technical review of all deliverables prior to submittal to AFCEC. Various communication drivers will trigger the need for communication among project personnel or stakeholders. The purpose of the table below is to present procedures that are in place for providing the appropriate notifications and generating the appropriate documentation when handling important communications, including those involving regulatory agencies, unexpected events, emergencies, non-conformances, and stop-work orders.

Communication Drivers	Responsible Affiliation	Name	Procedure
Task Modification Request	AFCEC PM	Catherine Jerrard	Document via Task Modification Request form
UFP-QAPP Amendments	AFCEC PM Amec Foster Wheeler PM Amec Foster Wheeler QAM	Catherine Jerrard Don Smallbeck Kevin Garrett	Amec Foster Wheeler PM send scope change to AFCEC PM. AFCEC PM send scope change to Air Force Contract Program office within 30 days
Site-Specific SAP Amendments	AFCEC PM Amec Foser Wheeler PM Amec Foster Wheeler QAM	Catherine Jerrard Don Smallbeck Kevin Garrett	Amec Foster Wheeler PM send scope change to AFCEC PM. AFCEC PM send scope change to Air Force Contract Program office within 30 days
Changes in Schedule	Amec Foster Wheeler PM	Don Smallbeck	Inform AFCEC PM of schedule impact letter as soon as impact is realized. Regulatory agencies will be notified during monthly BCT meeting of conference calls of significant changes to the schedule.
Issues in the Field that Result in Changes in Scope of Field Work	AFCEC PM Amec Foster Wheeler PM	Catherine Jerrard Don Smallbeck	Amec Foster Wheeler PM informs AFCEC PM; AFCEC PM issues scope change if warranted within 30 days; scope change to be implemented before work is executed. Regulatory agencies will be notified verbally and/or by email within 48 hours of significant issues that result in changes in scope of field work. Examples of significant issues include contaminant releases, or an accident requiring off-site care.

Communication Drivers	Responsible Affiliation	Name	Procedure
			Non-time critical variances (adjustments to planned work based on normal field variations and conditions) will be distributed in monthly BCT meetings or conference calls and documented in the project report.
Recommendations to Stop Work and Initiate Work upon CA	AFCEC PM Amec Foster Wheeler PM Amec Foster Wheeler QAM	Catherine Jerrard Don Smallbeck Kevin Garrett	Responsible Party immediately informs AFCEC PM
Analytical Data Quality Issues	TestAmerica PM Microbial Insights PM Amec Foster Wheeler Project Chemist Amec Foster Wheeler PM	Michelle Johnston Charles Slater Kevin Garrett Don Smallbeck	Lab PMs immediately notify Amec Foster Wheeler Project Chemist, Project QAM, and Amec Foster Wheeler PM if necessary

Notes:
AFCEC – Air Force Civil Engineer Center
Amec Foster Wheeler – Amec Foster Wheeler Environment & Infrastructure, Inc.
CA – Corrective Action
PM – Project Manager
QAM – Quality Assurance Manager
SAP – Sampling Analysis Plan
UFP-QAPP – Uniform Federal Policy Quality Assurance Project Plan
1. Microbial Insights PM included in the event that microbial analysis is deemed necessary to make project decisions.

Organizing team members across the country can be a challenging endeavor, especially when faced with communication obstacles and the requirements of shared document management. To make our team sharing more streamlined and efficient, the Amec Foster Wheeler team will access a SharePoint site to facilitate quick and relevant communication, manage shared documents with ease, and allow multiple layers of access control.

Our Former Williams AFB SharePoint team site is a collaboration platform where our team can store and share content with each other without technical or geographic limitations. The team site will primarily be for internal use but will have some functions that allow external use by the Air Force (AF), particularly for transfer of documents.

Through the SharePoint team site. Amec Foster Wheeler will access the following features.

- **Document libraries** - Manage shared documents with ease; use versioning to differentiate drafts from issued files; check-in and check-out ensures only one person is updating a file at any one time; use workflows to speed up document review/approval processes and set optional alerts to be notified when files change

- **News/announcements** - Post important announcements, that display right on the site's home page, and email all site users too if required
- **Calendars** - Stay organized using team calendars that allow you to publicize and manage team events; if you wish, synchronize the team calendar with Outlook
- **Task lists** - Assign action items to site users, making it painless for everyone on the team to update progress and track due dates
- **Searching** - Search capabilities search the site to help you find what you seek
- **CAD file collaboration** - Edit and review drawing files directly from the site; save time and effort with batch plotting; convert drawing files to a portable document format (PDF); also, whether or not users have a local installation of AutoCAD or MicroStation, any site user can plot/batch plot drawing files
- **Templates** - Ensure everyone in the team uses the correct document / CAD layout by publishing templates on the site
- **Document exchange** - Secure file exchange for internal and external users; automated notifications of file changes; layered security control for easy document sharing with clients

In addition to our SharePoint site, the core Amec Foster Wheeler team will hold various regularly scheduled teleconferences. The purpose of the teleconferences will be to discuss project status, upcoming project deliverables, resourcing needs, risk management issues, schedule, quality, and external communications. Each meeting always begins with a safety moment.

On a monthly basis, Don Smallbeck will conduct conference calls with dedicated cost and schedule control engineers to review the overall project progress on a site by site basis. This teleconference will be aimed at evaluating the earned value of the project, identify areas where the scheduled tasks may be falling behind, discuss critical path concerns, and agree on path forward action items to be communicated to both the project team as well as other team stakeholders. On a weekly basis, Don Smallbeck will hold a technical team conference call which will focus on the coordination of staff and staff assignments, discussion of technical project issues and concerns, review critical path tasks, discuss meetings and preparations, etc. These weekly calls will be joined by the entire project team to include the discipline leads (Stuart Pearson, Kevin Garrett, Jim Clarke, Chris Courtney, Natalie Chrisman, data management and Geographic Information System personnel, onsite Operation and Maintenance lead, and other project personnel as necessary). In addition to the aforementioned calls, periodic project meetings will be held at key junctures during the execution of the project. Most of these meetings will be held at local Amec Foster Wheeler offices but could be held at other locations depending on the site and discipline lead involved. Some of these face to face meetings could include Restoration Advisory Board and BRAC Cleanup Team preparation, design review meetings, and construction kick-off meetings.

QAPP WORKSHEET NO. 7 – PERSONNEL RESPONSIBILITIES AND QUALIFICATIONS TABLE

Name	Title/Role	Certifications and Registrations	Organizational Affiliation	Responsibilities
Catherine Jerrard	Project Manager		AFCEC	Oversee project, financial, schedule, and technical day-to-day management of the project.
Don Smallbeck	Project Manager/ Regulatory Lead		Amec Foster Wheeler	Oversee project to ensure compliance with project objectives, review documents and lead regulatory activities
Kevin Garrett	QA Lead; Project Chemist;	PhD, PE, PMP	Amec Foster Wheeler	Oversee laboratory QA/QC program to insure laboratory and data reporting QA/QC requirements are achieved.
Peter Guerra	EBR Design Lead	New Mexico Environment Certified Scientist	Amec Foster Wheeler	Refine model and associated design based on collected data.
Stuart Pearson	RD/RA Lead	PE	Amec Foster Wheeler	Coordinate with field lead to ensure that work is being conducted on schedule and not impacting other work on-site.
Natalie Chrisman	Investigation Lead	PE	Amec Foster Wheeler	Coordinate analytical laboratory subcontracts and resources. Day-to-day communication with the Field Lead and coordination with team for decisions.
Shanda Wagner, Emily Corkery, or Gwen Minnier	Field Lead		Amec Foster Wheeler	Implement Work Plan activities in the field. Coordinate push-pull testing, collection and shipping of samples, and management of generated groundwater.
Chad Barnes	Health & Safety	PE	Amec Foster Wheeler	Oversee project health and safety.
Michelle Barker	Data Manager		Amec Foster Wheeler	Project Data Management

Notes:
AFCEC – Air Force Civil Engineer Center
Amec Foster Wheeler – Amec Foster Wheeler Environment & Infrastructure, Inc.
PE – Professional Engineer
PMP – Project Management Professional
QA/QC – quality assurance/quality control
RD/RA – Remedial Design/Remedial Action
RPG – Registered Professional Geologist

There will be three primary subcontractors associated with the remedial action/site closure activities at ST012 as indicated below:

Subcontractor	Certifications and Registrations	Organizational Affiliation	Responsibilities
Remediation Equipment		TBD	Provide remediation equipment.
Analytical Laboratory	ADHS and DoD	TestAmerica	Perform laboratory analysis in accordance with the QAPP
Specialty Analytical Laboratory	None[1]	Microbial Insights, Inc.	Perform laboratory analysis in accordance with this QAPP if needed.

Notes:
TBD - to be determined
QAPP - Quality Assurance Project Plan
ADHS - Arizona Department of Health Services
DoD - Department of Defense
1. Microbial Insights, Inc. provides specialty molecular biology analyses to assess microbial populations; there are no certifications or accreditations available for this type of testing. Microbial Insights has been included in this QAPP/SAP in the event that microbial analyses are deemed necessary to make project decisions.

QAPP WORKSHEET NO. 8 – SPECIAL PERSONNEL TRAINING REQUIREMENTS TABLE

There is no specialized training associated with this work, other than the safety requirements described in the ST012 Health and Safety Plan (HASP). A Material Safety Data Sheet (MSDS) for sodium sulfate will be added to the ST012 HASP and will be reviewed prior to use.

QAPP WORKSHEET NO. 9 – PROJECT SCOPING SESSION PARTICIPANTS SHEET

Project Name: Enhanced Bioremediation at ST012 **Projected Date(s) of Sampling**: 2015 – 2017 **Project Manager**: Don Smallbeck, Amec Foster Wheeler	**Site Name**: Former Williams AFB **Site Location**: Mesa, Arizona

Date of Session: Beginning June 3, 2015 through September 24, 2015
Scoping Session Purpose: Weekly discussion for EBR design reporting and procurement.

Name	Affiliation and Title	Phone No.	E-mail Address
Stuart Pearson	Amec Foster Wheeler – Lead Engineer	207.828.3426	stuart.pearson@amecfw.com
Peter Guerra	Amec Foster Wheeler – Design Engineer	505.796.7291	peter.guerra@amecfw.com
Don Smallbeck	Amec Foster Wheeler – Project Manager	602.733.6040	donald.smallbeck@amecfw.com
Natalie Chrisman	Amec Foster Wheeler – Design Engineer	602.733.6087	natalie.chrisman@amecfw.com
Doug Fisher	Amec Foster Wheeler – Field Lead	602.733.6042	douglas.fisher@amecfw.com
John Anderson	Amec Foster Wheeler	207.828.2625	john.anderson2@amecfw.com
Stephanie Beadle	Amec Foster Wheeler – Staff Engineer	207.828.3408	stephanie.beadle@amecfw.com

Notes:
AFB – Air Force Base
Amec Foster Wheeler – Amec Foster Wheeler Environment & Infrastructure, Inc.

Comments/Decisions:

- Weekly meetings included discussions regarding terminal electron acceptor selection, injection/extraction strategy, groundwater model updates, proposed field activities, and steps for transitioning from SEE to EBR.
- A preliminary design was introduced and discussed during the September 2015 Base Realignment and Closure Cleanup Team meeting. The Enhanced Bioremediation slides presented to the EPA and ADEQ follow.

Action Items:

Prepare addendum to the RD/RAWP to supplement EBR design details.

Consensus Decisions:

Consensus decisions made during the weekly calls are included as part of the EBR design in the addendum to the RD/RAWP.

ATTACHMENT A

SITE ST012 ENHANCED BIOREMEDIATION UPDATE
BRAC CLEANUP TEAM MEETING – 15 SEPTEMBER 2015

Air Force Civil Engineer Center

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Former Williams Air Force Base

BRAC Cleanup Team Meeting
15 September 2015

Site ST012 Enhanced Bioremediation (EBR) Update

Site ST012 EBR Design

- **EBR design activities**
  - **Evaluated aerobic vs. sulfate reducing**
  - **Evaluated potential strategies to overlap EBR with final SEE injection/extraction phases**
  - **Evaluated injection strategies**
  - **Updated mass estimates, incorporating information from SEE wells and perimeter monitoring**
  - **Developing Phase 1 Injection Plan**

Site ST012 EBR Design

- **Aerobic vs. Sulfate Reducing Evaluation**

Terminal Electron Acceptor	Advantages	Disadvantages
Oxygen	• Proven at many sites for petroleum hydrocarbons • Faster degradation kinetics than sulfate	• Limited solubility, especially at higher temps, requires continuous delivery of peroxide over a long period
Sulfate	• **High solubility makes batch dosing feasible** • **Natural degradation at the Site is already dominated by sulfate reduction** • **Background sulfate concentrations will support ongoing natural attenuation during and after EBR**	• Slower degradation kinetics than oxygen

- **Sulfate selected over oxygen for the advantages**
- **Oxygen reserved as potential future supplement in recalcitrant areas**

Site ST012 EBR Design

- Evaluated Overlap of EBR with final SEE injection phase
- Considered co-injection of terminal electron acceptor (TEA) with steam near end of SEE injections
- Air co-injection with steam at steam injection well (SIW) for oxygen as TEA – ruled out based on selection of sulfate as primary TEA
- Sulfate solution injection in SIW – ruled out based on:
  - Would not deliver sulfate to areas of primary interest for EBR (areas untreated by/outside of SEE TTZ)
  - Temperatures in center of TTZ exceed mesophilic sulfate reducer limits. Population and ability of thermophilic sulfate reducers to degrade petroleum hydrocarbons unknown

Site ST012 EBR Design

- Evaluated Overlap of EBR with final SEE extraction phase
  - Considered TEA injection around site perimeter during final SEE extraction phase
  - Batch injections at perimeter wells would be pulled toward TTZs by final SEE extraction phase - ruled out based on:
    - Would not deliver sulfate to areas of primary interest for EBR (areas untreated by/outside of SEE TTZ)
    - Temperatures in center of TTZ exceed mesophilic sulfate reducer limits. Population and ability of thermophilic sulfate reducers to degrade petroleum hydrocarbons unknown

Site ST012 EBR Design

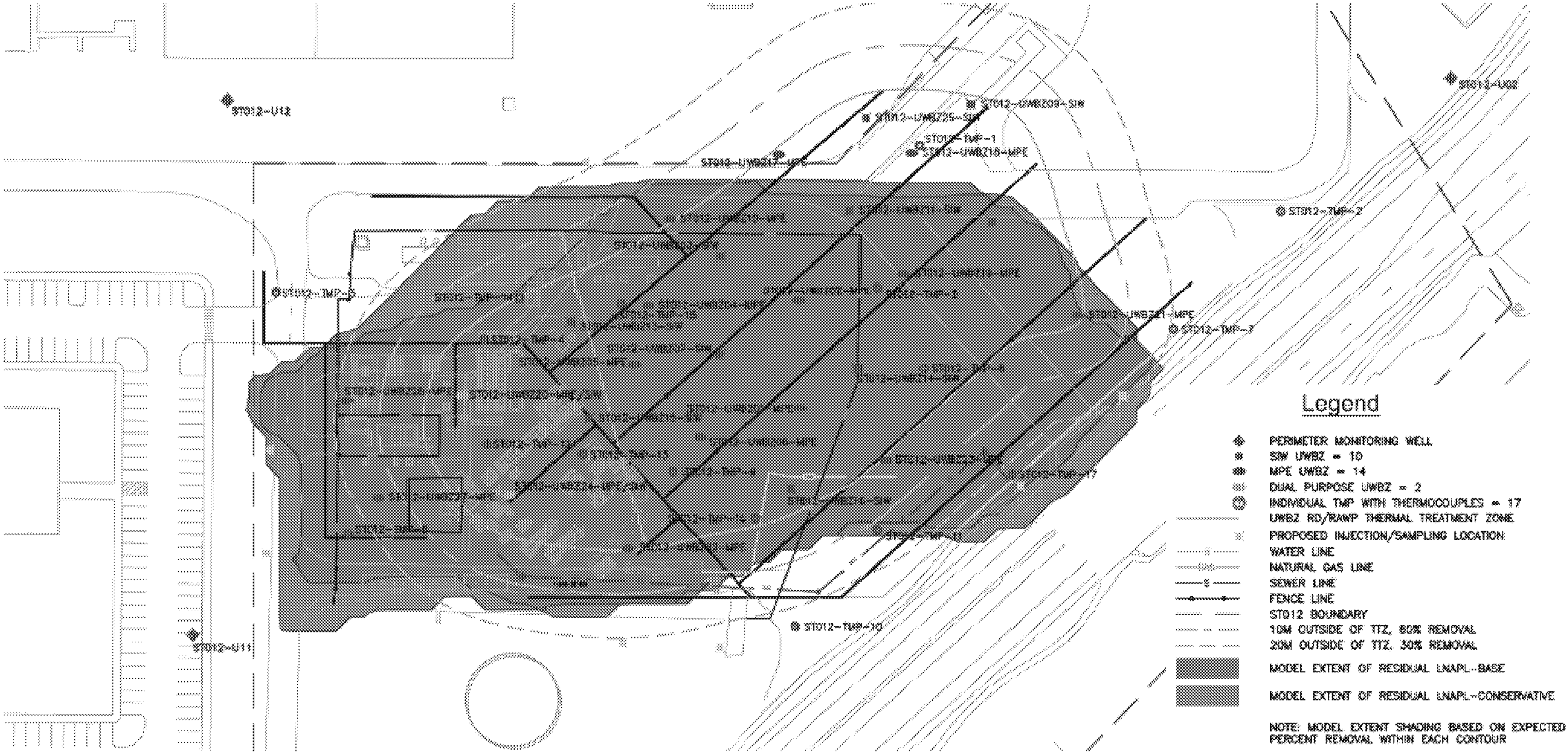
- Evaluated Injection Strategies
  - General Strategies Considered
    - Batch Injections
    - Batch Injections with extraction to help distribute
    - Recirculation
    - Recirculation to cross gradient sulfate fence followed by natural transport
- Initial strategy will focus on batch injections with extraction
- Will focus on areas of known and suspected mass outside the SEE TTZs
- Strategies will be dynamic, changing over time based on observed response
- Future use of any of the injection strategies is possible

Site ST012 EBR Design

- **Mass Estimate Update**
  - **Added boring log information from full-scale SEE well installation to existing PDI information**
  - **Updated volume estimates for pre-SEE treatment extent of LNAPL**
  - **Updated LNAPL mass calculations using volumes**
  - **Estimated benzene, ethylbenzene, toluene, xylenes, and naphthalene (BETX+N) mass based on observed mass fractions in extracted LNAPL**

Site ST012 EBR Design

- **Example Mass Extent with Discrete Treatment Zones – UWBZ (180 ft bgs)**



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Site ST012 EBR Design

- **Pre-SEE Mass Estimate Update Summary Table**
- **~18% reduction in mass estimate for base LNAPL interpretation**

		EBR Treatment Area Volume		Treatment Area Volume		Total Residual Volume	
Vertical Zone	NAPL Parameter	Based on Calculated Average LNAPL Residual	Based on Literature LNAPL Residual	Based on Calculated Average LNAPL Residual	Based on Literature LNAPL Residual	Based on Calculated Average LNAPL Residual	Based on Literature LNAPL Residual
2013 Base LNAPL Extent Interpretation Update							
Cobble Zone, Upper Water Bearing Zone, Low Permeability Zone, and Lower Saturated Zone	Remaining NAPL (pounds)	1,808,947	1,903,864	3,810,590	6,186,233	5,619,537	8,090,097
	Remaining BETX+N (pounds)	165,217	173,886	348,034	565,009	513,251	738,896
	Remaining Benzene (pounds)	6,590	6,936	13,881	22,536	20,471	29,471
2015 Base LNAPL Extent Interpretation Update							
Cobble Zone, Upper Water Bearing Zone, Low Permeability Zone, and Lower Saturated Zone	Remaining NAPL (pounds)	1,216,429	1,464,731	3,083,974	5,206,651	4,300,403	6,671,382
	Remaining BETX+N (pounds)	111,101	133,779	281,670	475,541	392,770	609,320
	Remaining Benzene (pounds)	4,431	5,336	11,234	18,967	15,666	24,303
2013 Conservative LNAPL Extent Interpretation Update							
Cobble Zone, Upper Water Bearing Zone, Low Permeability Zone, and Lower Saturated Zone	Remaining NAPL (pounds)	3,178,739	3,485,841	4,362,830	6,959,620	7,541,575	10,445,460
	Remaining BETX+N (pounds)	290,325	318,373	398,472	635,645	688,797	954,019
	Remaining Benzene (pounds)	11,580	12,698	15,893	25,353	27,473	38,051
2015 Conservative LNAPL Extent Interpretation Update							
Cobble Zone, Upper Water Bearing Zone, Low Permeability Zone, and Lower Saturated Zone	Remaining NAPL (pounds)	2,190,819	3,111,703	4,202,940	7,047,043	6,393,758	10,158,747
	Remaining BETX+N (pounds)	200,095	284,202	383,868	643,630	583,963	927,832
	Remaining Benzene (pounds)	7,981	11,335	15,311	25,671	23,292	37,007

BETX+N=benzene, ethylbenzene, toluene, xylenes, and naphthalene (based on mass fractions observed in recovered LNAPL)

Site ST012 EBR Design

- **Pre-EBR Mass Estimate Update**

  - Developed estimate for remaining mass using assumed removal rates from discrete treatment contours
    - Thermal Treatment Zone – 90%
    - Thermal Influence Zone – 60% (0 to ~10 m beyond the TTZ)
    - ROI Zone – 30% (~10 to ~20 m beyond the TTZ)
    - LPZ – 30% (within the TTZ footprint only)
  - Estimated total LNAPL removed at projected end of steam injection (31 October) using linear regression of data between 6 July and 17 August 2015 (representing a distinct change in LNAPL removal rate): 1,797,000 pounds (273,000 gallons)
  - Developed Calibration Ratio and applied between 2015 Base Mass Update calculations and projected SEE mass removed: 0.63
  - Added assumption of mass fraction reduction of volatile components within remaining LNAPL of 90% in TTZ and 25% in Thermal Influence Zone

Site ST012 EBR Design

- **Projected Pre-EBR mass remaining**

	LNAPL Removed (pounds)				BTEX + N Remaining (pounds)*					Benzene Remaining (pounds)*				
	TTZ	Thermal Influence	ROI	Untreated EBR	TTZ	Thermal Influence	ROI	Untreated EBR	Total	TTZ	Thermal Influence	ROI	Untreated EBR	Total
Base - Calculated														
Cobble Zone	47,544	8,203	975	0	48	375	208	94	725	2	15	8	4	29
Upper Water Bearing Zone	952,222	214,114	77,254	0	966	9,778	16,464	17,054	44,262	39	390	657	680	1,765
Low Permeability Zone	211,050	0	0	0	4,498	7,801	6,680	5,076	24,055	179	311	266	202	959
Lower Saturated Zone	1,348,078	66,234	6,216	0	1,368	3,025	1,325	2,162	7,879	55	121	53	86	314
Total	2,558,895	288,551	84,445	0	6,880	20,979	24,676	24,386	76,921	274	837	984	973	3,068
Adjusted for SEE Implementation Removal														
Cobble Zone	29,903	5,159	613	0	30	236	131	59	456	1	9	5	2	18
Upper Water Bearing Zone	598,899	134,667	48,589	0	608	6,150	10,355	10,726	27,838	24	245	413	428	1,110
Low Permeability Zone	132,740	0	0	0	2,829	4,907	4,201	3,193	15,130	113	196	168	127	603
Lower Saturated Zone	847,872	41,658	3,910	0	860	1,902	833	1,360	4,956	34	76	33	54	198
Total	1,609,413	181,484	53,112	0	4,327	13,194	15,520	15,338	48,379	173	526	619	612	1,930

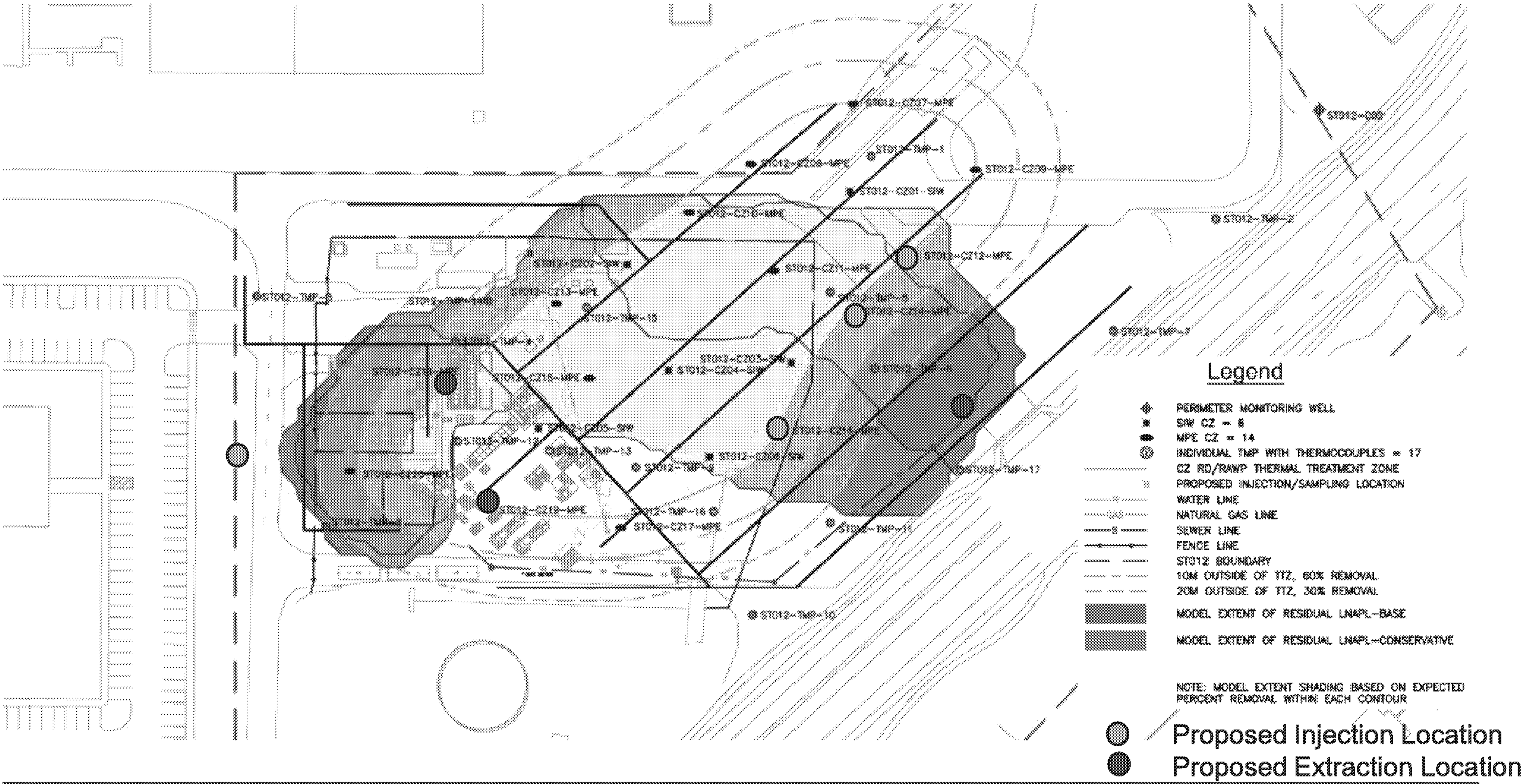
*fraction of BTEX+Naphthalene based on LNAPL analysis during SEE. Also assumes volatile fraction reductions of 90% in TTZ and 25% in thermal influence zone.

Site ST012 EBR Design

- Preliminary Phase 1 Injections
  - Focus on areas of highest mass outside of SEE TTZs
  - Use some existing perimeter monitoring wells
  - Install additional perimeter wells
  - Implement batch injections of sulfate solution in perimeter wells
  - Continue extraction from SEE perimeter wells to promote distribution of sulfate solution through contaminated zones
  - Monitor conditions and adjust

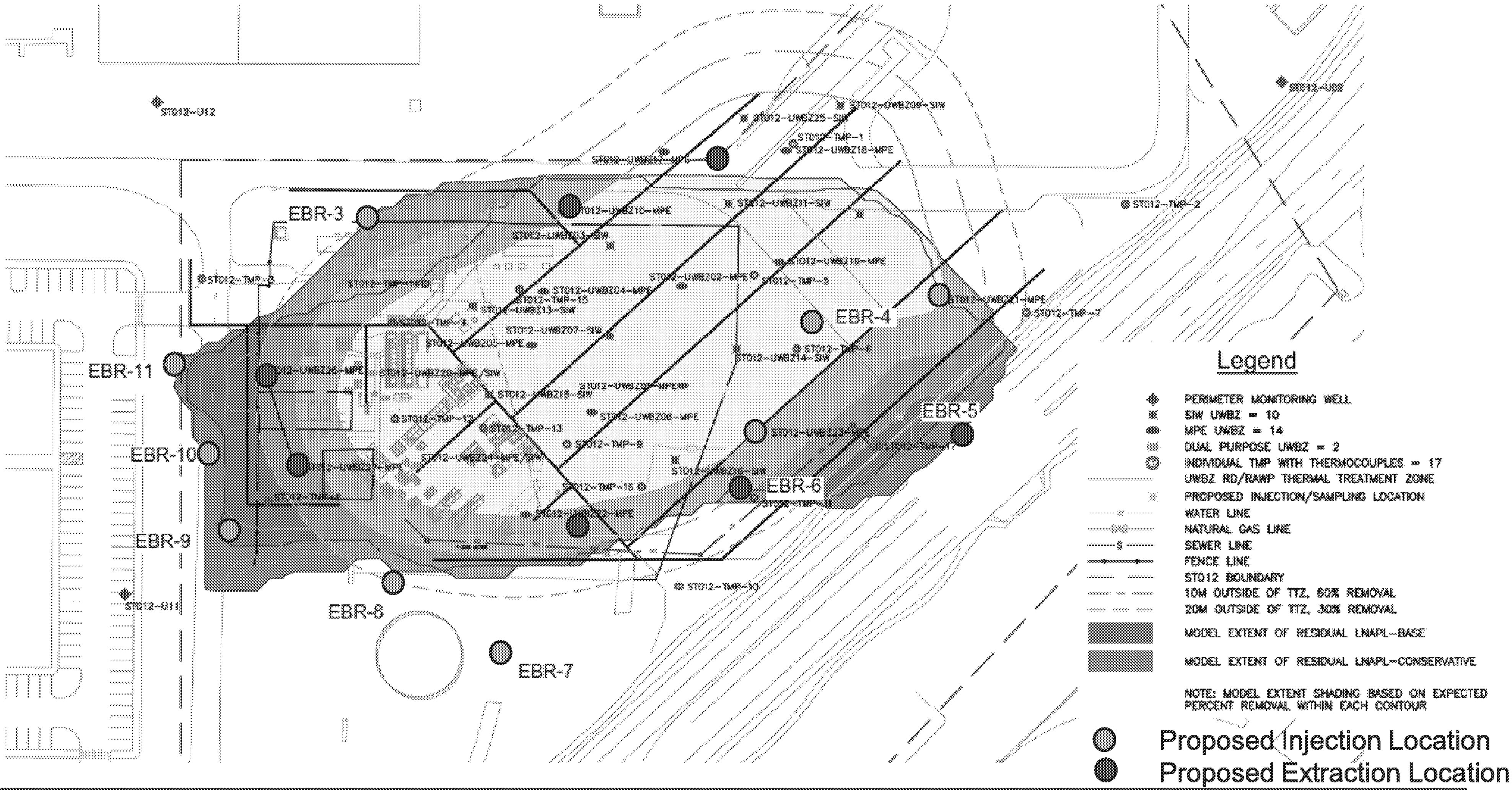
Site ST012 EBR Design

- **Phase I injection/extraction – CZ (160 ft bgs)**



Site ST012 EBR Design

- **Phase I injection/extraction – UWBZ (180 ft bgs)**



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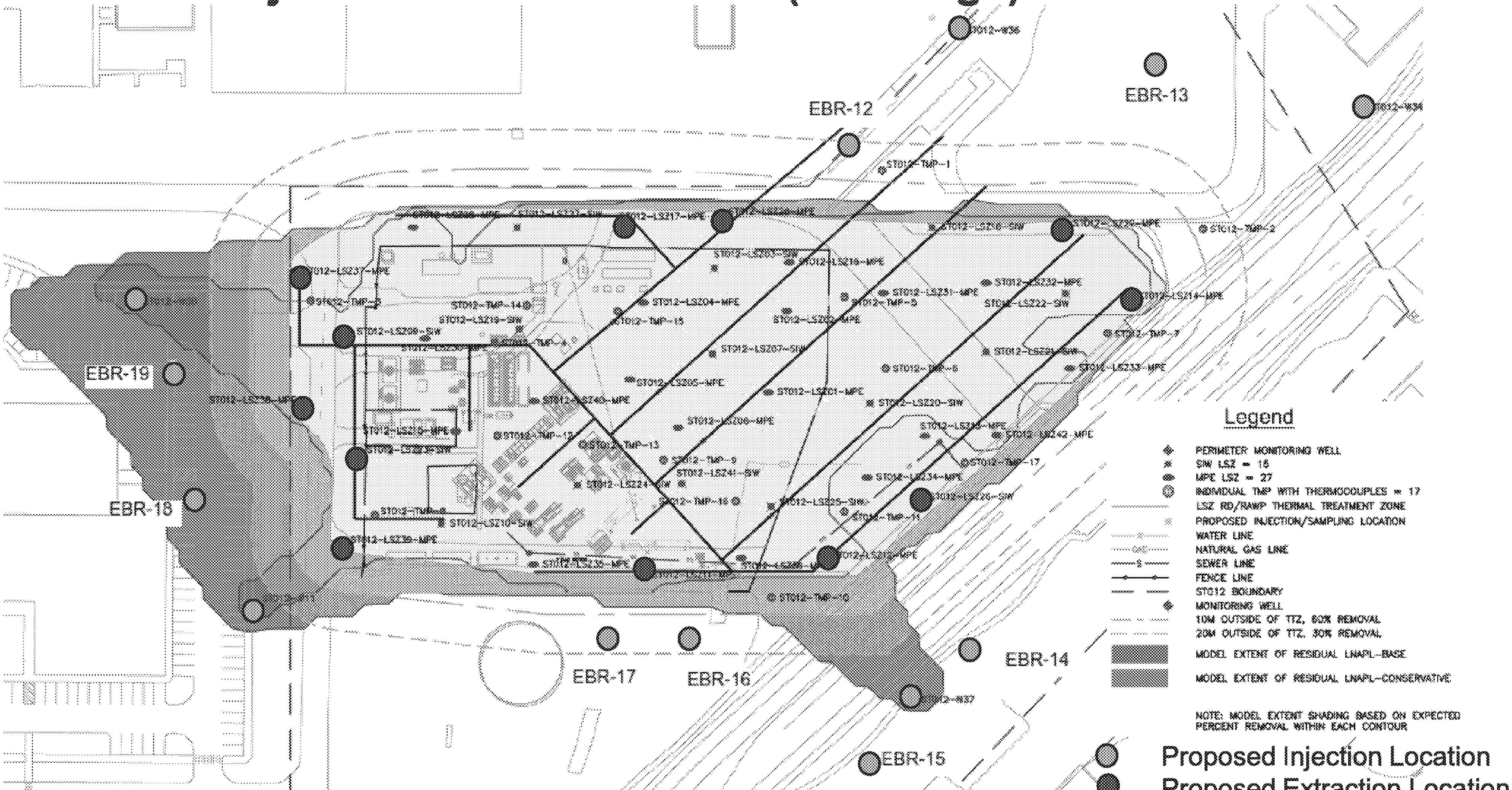
Site ST012 EBR Design

- **Phase I injection/extraction – LSZ (220 ft bgs)**



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Site ST012 EBR Design

- **Path Forward**
  - **Refine injection well locations and Phase I strategy**
  - **RD/RAWP Addendum #2 for EBR**
    - **Detail Phase I**
    - **Present methods for alternate injection strategies in the future – details of locations and volumes will be presented in future BCT meetings/calls**
  - **Implement Phase I**
    - **Begin drilling procurement in October**
    - **Injection timing depends on final SEE schedule and drilling completion**

QAPP WORKSHEET NO. 11 – PROJECT QUALITY OBJECTIVES/ SYSTEMATIC PLANNING PROCESS STATEMENTS

Project quality objectives (PQOs) define the type, quantity, and quality of data that are needed to answer specific environmental questions and support proper environmental decisions. To develop the PQOs, the DQO planning process described in the EPA "Guidance on Systematic Planning Using the DQOs Process, EPA QA/G-4" (EPA, 2006a) is used. The EPA QA/G-4 document suggests seven steps to be followed to develop project DQOs (performance and acceptance criteria) that clarify the study objectives, define the appropriate type of data, and specify tolerable levels of potential decision errors that will be used as the basis for establishing the quality and quantity of data needed to support environmental decisions.

Data Quality Objectives

Step 1 – Problem Definition

This Addendum to the RD/RAWP provides the design details and the remedial action implementation for the installation and operation of injection and extraction wells, as well as an extraction and treatment system to be operated during enhanced bioremediation activities at the site. The proposed sampling and investigation activities in this RD/RAWP are designed to achieve the following objectives:

- Verify compliance with extraction system discharge permits.
- Evaluate terminal electron acceptor (TEA) distribution at extraction wells.
- Evaluate progress of EBR and evaluate when to transition to Monitored Natural Attenuation.

Note, annual groundwater monitoring is addressed in the ST012 Groundwater Monitoring Work Plan.

Step 2 – Decision Statement

The data from the investigations, baseline sampling, and remedial performance monitoring prescribed in this Addendum to the RD/RAWP are being generated to support the installation and operation of injection and extraction wells, as well as an extraction and treatment system to be operated during enhanced bioremediation activities at the site.. Visual logs and soil and groundwater data will be generated from the investigation described in this Addendum. The data will be evaluated relative to the objectives identified in Worksheet #17.

The decision statements for this Addendum are:

- Is LNAPL present (either residual or free product) at the newly installed well locations prior to implementation of EBR? If present at a location, what is the vertical extent of the LNAPL?
- Do dissolved phase benzene, toluene, ethylbenzene, total xylenes, and naphthalene (BTEX+N) and TPH concentration data indicate that the natural flux of sulfate into the TTZ is effective for EBR or are additional TEA injections within the TTZ needed?

- Do system process samples indicate compliance with discharge requirements?
- Does the injection/extraction well configuration distribute the TEA within the formation to target remaining LNAPL at the perimeter of the TTZ?
- Do dissolved oxygen levels in target treatment areas reflect sulfate-reducing conditions?
- Have dissolved phase BTEX+N concentrations achieved the performance criteria for transition to MNA?

Step 3 – Decision Inputs

Field quantitative data (flow, groundwater elevations, oxidation reduction potential [ORP], dissolved oxygen [DO], etc.) and laboratory results will be the primary inputs for decisions relative to the use of sulfate as the TEA to remediate the groundwater anaerobically. Project-specific measurement and data management, validation criteria, and requirements are presented in the following list of worksheets:

- MPC are included for both field measurements and laboratory analyses (Worksheet No. 12);
- Project documentation will include a final report, Electronic Data Deliverables (EDDs), and recordkeeping (Worksheet No. 14);
- Reference limits and evaluation are presented in Worksheet No. 15;
- Sampling design and rationale are presented in Worksheet No. 17;
- Well locations and sampling methods are listed in tabular format in Worksheet No. 18;
- Analytical group, methods, and requirements for sample containers, preservation, and holding times are summarized in Worksheet No. 19;
- Field quality control (QC) is presented in Worksheet No. 20;
- The sample identification system, sample custody procedures (field and laboratory), and sample management and documentation will follow standard protocols as described in Worksheet No. 27;
- Data verification and validation will also follow standard protocols (Worksheets No. 34 through No. 36);
- The usability assessment process will be used to evaluate and document the usability (i.e., precision, accuracy, representativeness, completeness, comparability, and sensitivity [PARCCS]) of the data by considering the project DQOs, and whether the data are suitable for decision-making (Worksheet No. 37); and,
- QA management support is described in Worksheet No. 38.

Step 4 – Study Boundaries

The study areas of primary interest are areas of LNAPL contamination outside the SEE TTZs. Worksheet #17 provides the rationale for selection of study areas.

Step 5 – Decision Rules

A combination of qualitative data (e.g., visual logs and dye test kit results), quantitative data that provides a direct indication of LNAPL (e.g., TPH and benzene soil analytical results), and indirect quantitative data (e.g., PID readings, dissolved phase benzene and TPH concentrations) will be used to assess the horizontal and vertical presences of residual LNAPL. A combination of field data (e.g. flow, elevations, pH, ORP, DO) and laboratory data (e.g. cation/anion balance, total petroleum hydrocarbon [TPH] concentration) will be analyzed to determine the effectiveness of the TEA distribution and the TEA itself for the biodegradation of LNAPL.

Extraction wells will be regularly monitored for elevated sulfate concentrations to determine if TEA solution has reached the well. Confirmation of elevated sulfate concentrations (concentrations consistently exceeding baseline levels) will indicate the extraction well should be shut off to allow the TEA to remain within the formation. Elevated sulfate concentrations may also trigger a change in injection/extraction strategy and layout.

Additional design decisions that will be made cannot be reduced to a few simple decision rules that can be listed here. Decisions will be reached based on evaluations performed and documented in the field during well installation and EBR implementation. The groundwater model will be updated based on the hydraulic and biodegradation parameters, as well as trends in benzene, toluene, ethylbenzene, total xylenes, and naphthalene concentrations base on field data to aid in the decision to transition to MNA.

Step 6 – Limits on Decision Errors

Sufficient numbers of samples, appropriate analytical and field methods, and appropriate QA/QC protocols will be applied to minimize errors that may affect future use of the data and subsequent decision making. Analytical methods at the concentrations of interest are reliable. Qualitative data (e.g., visual records) and screening data (e.g., PID screenings) will supplement quantitative data (laboratory data) to limit decision errors.

Step 7 – Sample Design

The sample design and rationale are presented in Worksheet No. 17 and the sampling methods are identified in Worksheet #18 and the monitoring well locations are shown Figures 1-3 and 3-1 from the text.

QAPP WORKSHEET NO. 12 – MEASUREMENT PERFORMANCE CRITERIA

This worksheet has been subdivided by laboratory. TestAmerica generally follows EPA methods and associated QC, whereas Microbial Insights conduct specialty lab testing that follow their internal SOPs.

Measurement Performance Criteria Table – TestAmerica

Matrix	Water				
Analytical Groups	TPH; VOCs; Anions, ICP metals, Pesticides/PCBs, SVOCs				
Concentration Level	High				
Sampling Procedure	**Analytical Method / SOP**	**Data Quality Indicators**	**Measurement Performance Criteria**	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)**
SOP No. 10B	EPA Method 8260 – VOCs EPA Method 8270 - SVOCs EPA Method 8015B – TPH – (GRO+DRO) EPA Method 9056A – Anions, Ion Chroma-tography (Sulfate, nitrate) EPA Method 1699 – Pesticides by HRGC/HRMS	Precision	RPD of MS/MSD. See laboratory SOPs for acceptable RPDs for various test methods	Comparison of MS/MSD. Also comparison of field duplicate to parent sample.	A
		Accuracy/Bias	Varies pending method and QC sample type. See laboratory SOPs.	Laboratory method blanks, calibration verification samples, LCSs and matrix spikes.	A
		Accuracy/Bias – Contamination	No target analytes > quantitation limit	Equipment blank and field/trip blank.	S&A
		Representativeness	Contamination of sample or extract with a target analyte	Laboratory Method Blanks and field QC blanks.	S&A
		Comparability	Qualitative measure for field sampling and analytical procedures	Industry standard methods, QAPP compliance	S&A

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Matrix	**Water**
Analytical Groups	TPH; VOCs; Anions, ICP metals, Pesticides/PCBs, SVOCs
Concentration Level	High

Sampling Procedure	Analytical Method / SOP	Data Quality Indicators	Measurement Performance Criteria	QC Sample and/or Activity Used to Assess Measurement Performance	QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)
	EPA Method 6010B – ICP Metals[1] EPA Methods 8081/8082 – Pesticides/PCBs	Sensitivity	Verification of accurate assessment of data at the MDL where the MDL meets project objectives	In control calibrations, MBs, current and valid MDL for the matrix/method.	A
		Completeness	90-95%	Number of valid samples	S&A

[1]ICP Metals include: calcium, iron, magnesium, manganese, potassium and sodium.
DRO – diesel range organics
GRO – gasoline range organics
HRGC/HRMS – high resolution gas chromatography/high resolution mass spectrometry
ICP - inductively coupled plasma
JP-4 – jet petroleum grade 4
LCS - laboratory control samples
MDL – method detection limit
MS/MSD – matrix spike/matrix spike duplicate
PCBs – polychlorinated biphenyls
QAPP – Quality Assurance Project Plan
QC – quality control
RPD – relative percent difference
SOP – standard operating procedure
SVOCs – semi-volatile organic compounds
TPH – total petroleum hydrocarbons
VOC – volatile organic compound

Measurement of Performance Criteria Table – Microbial Insights

Matrix	**Water**				
Analytical Group	Functional genes associated with denitrifying bacteria, *Geobacter* species, sulfate reducing bacteria and methanogens; microbial consortia footprint				
Concentration Level	**High**				
Sampling Procedure	**Analytical Method / SOP**	**Data Quality Indicators**	**Measurement Performance Criteria**	**QC Sample and/or Activity Used to Assess Measurement Performance**	**QC Sample Assesses Error for Sampling (S), Analytical (A), or both (S&A)**
N/A	Quantitative Polymerase Chain Reaction Analysis Phospholipid Fatty Acid Analysis	Precision	CT value with ±20% of known value	Laboratory control sample duplicates.	A
		Accuracy/Bias	Standard curve R^2 >0.99, CT value with ±20% of known value	Initial Assay Calibration, continued calibration verification	A
		Accuracy/Bias – Contamination	Lower than quantitation limit	Trip, field, and method blanks	S&A

Notes:
QC – quality control
SOP – standard operating procedure

QAPP WORKSHEET NO. 15 – REFERENCE LIMITS AND EVALUATION

The analytes listed in the following tables will be analyzed using EPA analytical methods. The analyses will be performed in accordance with EPA SW-846 (EPA, 2008) and laboratory SOPs. Reporting limits (RLs) will be dependent on the technical limitations of the analytical methods and matrices. The laboratory will conduct studies to establish method detection limits (MDLs) or limits of detection (LODs) and limits of quantitation (LOQs) for each analyte listed in the tables below. The MDLs, LODs, and LOQs will be as low as practically achievable for any given matrix. Every effort will be made to have the detection limit lower than the maximum contaminant level or site-specific cleanup criteria if applicable.

TestAmerica Parameters, Method Limits, and Associated Site-Specific Cleanup Criteria (Groundwater)

Analysis	Method	Parameter	CAS Number	Target Reporting Limits Water - µg/L	Approximate MDLs Water - µg/L	Project Action Levels[1] Water - µg/L
Volatile Organic Compounds	8260B	1,2,4-Trimethylbenzene	95-63-6	1.0	0.14	NA
		1,2-Dichloroethane	107-06-2	1.0	0.13	5
		1,3,5-Trimethylbenzene	108-67-8	1.0	0.14	NA
		Benzene	71-43-2	1.0	0.16	5
		Carbon disulfide	75-15-0	2.0	0.45	NA
		cis-1,2-Dichloroethene	156-59-2	1.0	0.15	NA
		Cyclohexane	110-82-7	2.0	0.28	NA
		Ethylbenzene	100-41-4	1.0	0.16	700
		Isopropylbenzene	98-82-8	1.0	0.19	NA
		Methyl tert-butyl ether	1643-04-4	5.0	0.25	NA
		Methylcyclohexane	108-87-2	2.0	0.36	NA
		Methylene Chloride	75-09-2	5.0	0.32	5.0
		m-Xylene and p-Xylene	108-38-3, 106-42-3	2.0	0.34	NA
		Naphthalene	91-20-3	1.0	0.22	28
		n-Butylbenzene	104-51-8	1.0	0.32	NA
		n-Hexane	110-54-3	2.0	0.42	NA
		n-Propylbenzene	103-65-1	1.0	0.16	NA
		o-Xylene	95-47-6	1.0	0.19	NA
		p-Isopropyltoluene	99-87-6	1.0	0.17	NA
		sec-Butylbenzene	135-98-8	1.0	0.17	NA
		tert-Butylbenzene	98-06-6	1.0	0.16	NA
		Tetrachlorethene	127-18-4	1.0	0.20	5
		Toluene	108-88-3	1.0	0.17	1,000
		Trichloroethene	79-01-6	1.0	0.16	NA
		Trichlorofluoromethane	75-69-4	2.0	0.29	1,100
		Vinyl chloride	75-01-4	1.5	0.10	NA

Analysis	Method	Parameter	CAS Number	Target Reporting Limits Water - µg/L	Approximate MDLs Water - µg/L	Project Action Levels[1] Water - µg/L
		Total Xylenes	various	2.0	0.19	10,000
Semi-volatile Organic Compounds	8270C	1,2,4-Trichlorobenzene	120-82-1	10	3.6	NA
		1,2-Dichlorobenzene	95-50-1	10	2.9	NA
		1,3-Dichlorobenzene	541-73-1	10	3.4	NA
		1,4-Dichlorobenzene	106-46-7	10	3.3	NA
		2,4,5-Trichlorophenol	95-95-4	21	2.7	NA
		2,4,6-Trichlorophenol	88-06-2	21	2.9	NA
		2,4-Dichlorophenol	120-83-2	10	3.5	NA
		2,4-Dimethylphenol	105-67-9	10	5.4	NA
		2,4-Dinitrophenol	51-28-5	52	20	NA
		2,4-Dinitrotoluene	121-14-2	10	8.2	NA
		2,6-Dinitrotoluene	606-20-2	10	6.1	NA
		2-Chloronaphthalene	91-58-7	10	2.3	NA
		2-Chlorophenol	95-57-8	10	4	NA
		2-Methylnaphthalene	91-57-6	10	2.8	27
		2-Methylphenol	95-48-7	10	3.2	720
		2-Nitroaniline	88-74-4	10	7.5	NA
		2-Nitrophenol	88-75-5	16	5.9	NA
		3,3'-Dichlorobenzidine	91-94-1	10	3.2	NA
		3-Nitroaniline	99-09-2	10	6.7	NA
		4,6-Dinitro-2-methylphenol	534-52-1	52	19	NA
		4-Bromophenyl phenyl ether	10-55-3	10	2.8	NA
		4-Chloro-3-methylphenol	59-50-7	10	2.9	NA
		4-Chloroaniline	106-47-8	10	2.3	NA
		4-Chlorophenyl phenyl ether	7005-72-3	10	2.5	NA
		4-Nitroaniline	100-01-6	10	3.3	NA

Analysis	Method	Parameter	CAS Number	Target Reporting Limits Water - µg/L	Approximate MDLs Water - µg/L	Project Action Levels[1] Water - µg/L
		4-Nitrophenol	100-02-7	26	9.5	NA
		Acenaphthene	83-32-9	10	2.2	NA
		Acenaphthylene	208-96-8	10	2.2	NA
		Anthracene	120-12-7	10	2.3	NA
		Benzo[a]anthracene	56-55-3	10	2.3	NA
		Benzo[a]pyrene	50-32-8	10	2.3	NA
		Benzo[b]fluoranthene	205-99-2	10	2.2	NA
		Benzo[g,h,i]perylene	191-24-2	10	3.7	NA
		Benzo[k]fluoranthene	207-08-9	10	2.7	NA
		Benzoic acid	65-85-0	26	13	NA
		Benzyl alcohol	100-51-6	10	4.3	NA
		bis (2-chloroisopropyl) ether	108-60-1	10	3	NA
		Bis(2-chloroethoxy)methane	111-91-1	10	2.9	NA
		Bis(2-chloroethyl)ether	111-44-4	10	2.6	NA
		Bis(2-ethylhexyl) phthalate	117-81-7	10	3.1	NA
		Butyl benzyl phthalate	85-68-7	10	2.3	NA
		Chrysene	218-01-9	10	2.4	NA
		Dibenz(a,h)anthracene	53-70-3	10	4.2	NA
		Dibenzofuran	132-64-9	10	2.3	NA
		Diethyl phthalate	84-66-2	10	2.7	NA
		Dimethyl phthalate	131-11-3	21	5.1	NA
		Di-n-butyl phthalate	84-74-2	10	2.6	NA
		Di-n-octyl phthalate	117-84-0	10	2.5	NA
		Fluoranthene	206-44-0	10	2.7	NA
		Fluorene	86-73-7	10	2.3	NA

Analysis	Method	Parameter	CAS Number	Target Reporting Limits Water - µg/L	Approximate MDLs Water - µg/L	Project Action Levels[1] Water - µg/L
		Hexachlorobenzene	118-74-1	10	2.5	NA
		Hexachlorobutadiene	87-68-3	10	5.9	NA
		Hexachloroethane	67-72-1	10	3.9	NA
		Indeno[1,2,3-cd]pyrene	193-39-5	10	3.6	NA
		Isophorone	78-59-1	10	2.7	NA
		m & p - Cresol	15831-10-4	10	6	NA
		Nitrobenzene	91-20-3	10	2.5	NA
		N-Nitrosodi-n-propylamine	98-95-3	10	3.3	NA
		N-Nitrosodiphenylamine	621-64-7	10	2.5	NA
		Pentachlorophenol	86-30-6	52	14	NA
		Phenanthrene	87-86-5	10	2.3	NA
		Phenol	85-01-8	10	3.9	4,200
		Pyrene	108-95-2	10	2.2	NA
Total Petroleum Hydrocarbon	8015B	Gasoline Range Organics	various	25	10	NA
		Diesel Range Organics		250	32.6	NA
Pesticides	8081	4,4'-DDE	72-55-9	0.054	0.0070	NA
		4,4'-DDT	50-29-3	0.054	0.0070	NA
		Aldrin	309-00-2	0.054	0.0075	NA
		Alpha BHC	319-84-6	0.054	0.012	NA
		Beta BHC	319-85-7	0.054	0.0080	NA
		Gamma BHC	58-89-9	0.054	0.0070	NA
		Heptachlor	76-44-8	0.054	0.015	NA
		Heptachlor epoxide	1024-57-3	0.054	0.0072	NA
Polychlorinated Biphenyls	8082	PCB-1016	12674-11-2	1.1	0.18	NA
		PCB-1221	11104-28-2	1.1	0.22	NA
		PCB-1232	11141-16-5	1.1	0.37	NA
		PCB-1242	53469-21-9	1.1	0.49	NA
		PCB-1248	12672-29-6	1.1	0.19	NA

Analysis	Method	Parameter	CAS Number	Target Reporting Limits Water - µg/L	Approximate MDLs Water - µg/L	Project Action Levels[1] Water - µg/L
		PCB-1254	11097-69-1	1.1	0.30	NA
		PCB-1260	11096-82-5	1.1	0.16	NA
Anions (Ion Chromatography)	9056A	Sulfate	7778-80-5	5000	232	NA
		Nitrate				
ICP Metals	6010C	Calcium	7440-70-2	200	34.5	NA
		Iron	7439-89-6	100	22	NA
		Magnesium	7439-95-4	100	14	NA
		Manganese	7439-96-5	10	0.253	NA
		Potassium	7440-09-7	500	63	NA
		Sodium	7440-23-5	1000	140	NA
HRGC/HRMS Pesticides	1699	4,4'-DDE	72-55-9	0.0004	EDL[3]	NA
		4,4'-DDT	50-29-3	0.0004	EDL[3]	NA
		Aldrin	309-00-2	0.0004	EDL[3]	NA
		Alpha BHC	319-84-6	0.0004	EDL[3]	NA
		Beta BHC	319-85-7	0.0004	EDL[3]	NA
		Gamma BHC	58-89-9	0.0004	EDL[3]	NA
		Heptachlor	76-44-8	0.0004	EDL[3]	NA
		Heptachlor epoxide	1024-57-3	0.0004	EDL[3]	NA

Notes:

[1]Project action levels listed based on OU-2 ROD Amendment 2 cleanup levels.
[2]There are no target limits associated with LNAPL analysis.
3 For each investigative sample, an estimated detection limit (EDL) is determined. Further discussion is included in the Method 1699 SOP included in Attachment B
µg/L - micrograms per liter
CAS - Chemical Abstract Service
EDL – estimated detection limit
MDL - method detection limit
NA - not applicable

Microbial Insights Target Analytes and Method Limits (Water)

Analysis	Method	Parameter	Limit of Quantitation	Limit of Detection
qPCR	qPCR	Denitrifying bacteria (cells/sample)	5000	100
		Geobacter (cells/sample)	5000	100
		Sulfate reducing bacteria (SRB) (cells/sample)	5000	100
		Methanogenic bacteria (cells/sample)	5000	100
PLFA	PLFA	Cells (cells/sample)	1×10^7	3×10^6
		Firmicutes (TerBrSats)	N/A	N/A
		Proteobacteria (Monos)	N/A	N/A
		Anaerobic Metal Reducers (BrMonos)	N/A	N/A
		SRB/Actinomycetes (MidBrSats)	N/A	N/A
		General (Nsats)	N/A	N/A
		Eukaryotes (polyenoics)	N/A	N/A
		Slowed Growth	N/A	N/A
		Decreased Permeability	N/A	N/A

Notes:
qPCR – quantitative polymerase chain reaction
PLFA – phospholipid fatty acid

QAPP WORKSHEET NO. 17 – SAMPLING DESIGN AND RATIONALE

The proposed sampling and investigation activities in this RD/RAWP are designed to achieve the following objectives:

- Supplement existing data on subsurface geology and LNAPL distribution during remedial construction to support development of the remedial operational strategies during implementation of the design.
- To collect operational data to verify compliance with permits and, where permits are not formally required to verify compliance with substantive requirements.
- To monitor progress of remediation support decision making regarding transition to MNA
- Evaluate terminal electron acceptor (TEA) distribution at extraction wells.
- Evaluate progress of EBR and determine when to transition to Monitored Natural Attenuation.

EBR baseline and performance monitoring will be conducted to provide data for evaluation of EBR progress. Monitoring of EBR operation will include a combination of process monitoring (e.g., pressures, flow rates) and analytical monitoring for TEA distribution, microbial activity, and dissolved concentrations of site COCs to evaluate the progression of EBR. This section discusses the performance monitoring specific to the EBR implementation. Table 17.1 summarizes the monitoring, sampling, and analysis methods and frequencies. Sampling programs are further discussed in the following subsections.

Table 17.1 EBR Sampling Summary Table

Media	Locations	Monitoring/ Analysis	Frequency	Sample Purpose
Baseline				
• Liquid	• Select SIWs and MPE wells (as listed in Table 4-2). • All newly installed injection and extraction wells (as listed in Table 4-1)	• VOCs (8260B) • SVOCs (8270) • ICP Metals (6010C) • Nitrate and Sulfate (9056A) • Alkalinity (SM 2320B) • Sulfate field screening	• Single event near the end of post-steam extraction activities (existing wells) • At least one week after well development (new wells)	• Performance (Baseline) • Operational Strategy Assessment (adjustments to TEA injection/ extraction strategy)
• Soil	• All drilled locations (drilled using sonic)	• Continuous logging • PID readings	• Approximate 10-foot vertical core intervals or where changes are noted.	• Operational Strategy Assessment (injection/ extraction strategy)
		• LNAPL Dye Test Kits	• At core intervals of suspected LNAPL based on odor, staining, or PID readings	• Operational Strategy Assessment (injection/ extraction strategy)

Table 17.1 EBR Sampling Summary Table				
Media	**Locations**	**Monitoring/ Analysis**	**Frequency**	**Sample Purpose**
		• VOCs (EPA 8260B) • TPH (8015B)	• 1 per 10 ft interval where dye test kit is positive	• Operational Strategy Assessment (confirmation of qualitative monitoring/ analysis)
Injection Well and Injection Solution Sampling				
• Liquid	• TEA Injection fluid	• ICP Metals (6010C) • Sulfate (9056A)	• Monthly	• Operational Strategy (verification of TEA concentration)
• Liquid	• New and existing injection locations (24) (as listed in Tables 4-1 and 4-2)	• VOCs (8260B) • ICP Metals (6010C) • Sulfate and Nitrate (9056A)	• Quarterly	• Performance (dissolved VOCs reduction, TEA solution distribution, dissolved metals monitoring)
Extraction Well Sampling				
• Liquid	• New and existing extraction locations (24) (as listed in Tables 4-1 and 4-2 except sampling frequency is higher for wells in next row)[2]	• VOCs (8260B)	• Quarterly	• Performance (dissolved COCs reduction) • Operational Strategy Assessment (bioactivity and TEA distribution)
		• TPH (8015B) • ICP Metals (6010C)	• Semiannual	• Performance • Compliance (trace metals monitoring)
		• Sulfate Field Screening • Sulfate (9056A)	• Biweekly during the first month (sulfate only), then transition to monthly thereafter with confirmatory offsite laboratory analysis (9056A) for every 10% of field screening samples • Monthly at extraction wells once extraction turned off • pH and temperature monitoring will stop following shutoff of extraction well	• Operational Strategy Assessment (TEA distribution)
• Liquid	Select extraction wells: • ST012-CZ18 • ST012-CZ19 • ST012-CZ21 • ST012-UWBZ31	• Sulfate Field Screening • Sulfate (9056A)	• Weekly during the first two months, then transition to monthly thereafter with confirmatory offsite laboratory analysis for	• Operational Strategy Assessment (TEA distribution)

Table 17.1 EBR Sampling Summary Table				
Media	**Locations**	**Monitoring/ Analysis**	**Frequency**	**Sample Purpose**
	• ST012-LSZ39		every 10% of field screening samples	
Groundwater Monitoring Well Sampling				
• Liquid	Groundwater monitoring wells[2]: • ST012-C02 • ST012-U02 • ST012-W12 • ST012-U37 • ST012-RB-3A • ST012-W24 • ST012-U38 • ST012-W38 • ST012-U12 • ST012-CZ01 • ST012-CZ05 • ST012-UWBZ19 • ST012-UWBZ24 • ST012-LSZ21 • ST012-LSZ27	• VOCs (8260B) • ICP Metals (6010C) • Sulfate (9056A) •	• Quarterly	• Performance (dissolved COCs reduction) • Operational Strategy Assessment (TEA distribution)
• Liquid	• Annual Groundwater Monitoring Locations (see AMEC, 2013b with modified locations per Table 5-3 of the RD/RAWP)	• See AMEC, 2013b with modified locations per Table 5-3 of the RD/RAWP.	• Annual	• Compliance (RODA 2)
Process Water Sampling				
• Liquid	• Treatment System Influent	• VOCs (8260B)	• Monthly	• Performance (mass removal)
• Liquid	• GAC Influent • GAC Midfluent • GAC Effluent	• VOCs (8260B)[1]	• Weekly for influent and midfluent until influent concentrations stabilize, then monthly, quarterly at effluent	• Performance (mass removal by GAC) • Operation (breakthrough at Midfluent) • Compliance (effluent discharge permit)
		• SVOCs (8270)[1]	• Monthly[1]	
		• Pesticides/PCBs (8081/8082)[1] • HRGC/HRMS (1699)	• 8081/8082 Monthly with a second sample sent for HRGC/HRMS analysis if there are any detections of prohibited compounds[1]	

Table 17.1 EBR Sampling Summary Table				
Media	Locations	Monitoring/ Analysis	Frequency	Sample Purpose
	• Effluent Discharge	• Liquid Discharge Flow Rate	• Daily flow meter readings[1]	• Compliance (effluent discharge permit)

Notes:
[1]May be modified based on final discharge permit.

[2]Water quality parameters (pH, temperature, DO, and ORP) will be evaluated at each sampled well using a flow through cell and calibrated probes

ASTM – American Society for Testing Materials
DO – dissolved oxygen
FID – flame ionization detector
GAC – granular activated carbon
GC – gas chromatograph
HRGC/HRMS – high resolution gas chromatography /high resolution mass spectrometry
LNAPL – light non-aqueous phase liquid
LSZ – lower saturated zone
MPE – multiphase extraction
ORP – oxidation reduction potential
PCBs – polychlorinated biphenyls
PID – photoionization detector
PLC – programmable logic controller
SEE – steam enhanced extraction
TPH – total petroleum hydrocarbons
VOCs – volatile organic compounds

Baseline Sampling

Prior to EBR injection and extraction activities, sampling will be conducted to determine baseline conditions and to adjust operational strategy based on conditions in the field.

Pre-EBR Groundwater Sampling

During the final stages of SEE at the site, MPE wells will be sampled to determine baseline dissolved BTEX+N concentrations within the TTZ at the site. After drilling and well construction activities for new injection and extraction wells are complete, Amec Foster Wheeler will perform an initial round of groundwater sampling to document baseline conditions in the EBR treatment area prior to EBR activities. The following analyses by laboratory will be conducted at all newly installed wells and select MPE wells at the site:

- Sulfate (EPA Method 9056A)
- ICP Metals (EPA Method 6010C)
- VOCs (EPA Method 8260B)
- SVOCs (EPA Method 8270C)

Baseline sampling will also help evaluate potential adjustments to the injection/extraction strategy.

Soil Characterization for LNAPL

As discussed in Worksheet 11, all new well cores will be screened with a PID for the presence of VOCs. Dye test kits will be used to confirm LNAPL presence/absence that is suspected based on visual and PID screening. The selection of a core interval for dye testing will be subject to the judgement of the field geologist and will depend on the uncertainty associated with the visual and PID screening methods. It is anticipated that the frequency of dye test kit use will decrease over the investigation period as confidence in visual and PID readings increases. Soil samples with positive dye test kit results will be sent off site for analysis of VOCs by EPA Method 8260B and TPH (sum of gasoline range organics [GRO] and diesel range organics [DRO]) by EPA Method 8015B. Results of LNAPL characterization will be used to make adjustments to screened intervals, well layout, and the TEA injection/extraction strategy.

Injection Well and Injection Solution Sampling

Sampling at individual existing and new injection wells and the injection solution will be used to monitor dissolved VOC concentrations, dissolved metal concentrations, and sulfate concentrations. Injection monitoring will help assess and necessary changes to injection/extraction strategy.

TEA Injection Solution Sampling

On a monthly basis, TEA injection solution samples will be collected to confirm injection solution concentration. TEA injection solution will be analyzed on a monthly basis for dissolved metals concentrations via EPA Method 6010C to confirm quality assurance reports received from the TEA supplier regarding the arsenic concentration in TEA.

Injection Well Sampling

Each existing and new injection well will be sampled and analyzed for VOCs via EPA Method 8260B, dissolved metals vis EPA Method 6010C, and for sulfate and nitrate via EPA Method 9056A to monitor: TEA distribution, progress in reduction of dissolved VOCs, and any changes in dissolved metals within the formation that may have resulted from TEA solution injections.

Extraction Well Sampling

During EBR activities, each extraction well (24 wells total) will be sampled and analyzed for VOCs (BTEX+N) via EPA Method 8260B. BTEX+N monitoring at individual extraction wells will help document progress towards the transition to MNA.

On a semiannual basis, all 24 extraction wells will be sampled and analyzed for TPH via EPA Method 8015B and ICP Metals via EPA Method 6010C. TPH will be monitored to document the general changes in groundwater petroleum hydrocarbons beyond the COCs. ICP Metals analysis will be conducted to document any changes in dissolved metals within the formation that may have resulted from TEA solution injections.

Extracted groundwater from individual wells will be monitored throughout EBR activities to determine if and at what rate TEA is being distributed between injection and extraction points. Based on groundwater model results, TEA travel times will vary between different injection/extraction well pairs. The following extraction wells are predicted to have a short timeframe (less than two months) to TEA breakthrough and will be monitored on a weekly basis using sulfate field test kits:

- ST012-CZ18
- ST012-CZ19
- ST012-CZ21-EBR

- ST012-UWBZ31
- ST012-LSZ39

In addition, 10% of sulfate field test kit samples will also be analyzed for sulfate offsite via EPA Method 9056A to verify field test results. The remaining 19 extraction wells will be monitored on a biweekly basis for the first 3 months, then will transition to monthly sampling thereafter. Following TEA breakthrough, each extraction well will continue to be sampled and analyzed via the sulfate field test kits on a monthly basis with 10% of samples being sent offsite for sulfate analysis. Modifications to the field test kit/laboratory analysis may be proposed based on the correlations between these methods observed.

Groundwater Monitoring Well Sampling

Monitoring wells will be used as sampling locations to provide additional dissolved groundwater concentrations data throughout the site.

Perimeter monitoring wells (including those being used as injection points) will also be gauged for LNAPL on a monthly basis for the first six months of EBR activities, and will transition to a quarterly basis thereafter.

Quarterly Groundwater Monitoring

Samples from 10 perimeter monitoring wells and six select MPE wells/SIWs within the TTZ will be analyzed for the following on a quarterly basis:

- VOCs (BTEX+N) via EPA Method 8260B
- ICP Metals via EPA Method 6010C
- Sulfate via EPA Method 9056A
- TPH via EPA Method 8015B

Annual Groundwater Monitoring

Annual groundwater monitoring will continue at the site in accordance with the Groundwater Monitoring Work Plan (AMEC, 2013b).

Process Water Sampling

Liquid samples will be collected from the GAC influent and midfluent to monitor for contaminant breakthrough. Liquid samples will be submitted for laboratory analysis for VOCs via EPA Method 8260B on a weekly basis.

Liquid samples will be collected from the GAC effluent to monitor for contaminant breakthrough and to document discharge compliance. Liquid samples will be submitted for laboratory analysis for the following:

- VOCs via EPA Method 8260B on a monthly basis
- Pesticide/polychlorinated biphenyls via EPA SW846 Method 8081/8082 on a monthly basis

- HRGC/HRMS via EPA Method 1699 (when necessary to verify any pesticides detections that may occur)
- Semi-volatile organics via EPA Method 8270C on a monthly basis

These analyses are subject to change pending updates to the sewer discharge permit.

In addition to chemical analysis, discharge flow rate will be monitored via daily flow meter readings to ensure compliance with the maximum daily discharge flowrate as designated in the sewer discharge permit.

QAPP WORKSHEET NO. 18 – SAMPLING LOCATIONS AND METHODS/SOP REQUIREMENTS TABLE

The sampling locations and specific methods and SOPs are listed in Tables 18.1 through 18.7. Groundwater samples will be collected at least one week after well development. Attachment A of the Program QAPP provides the program sampling SOPs (AMEC, 2012c). Project-specific SOPs were provided in Appendix H of the RD/RAWP.

Table 18.1 – Baseline Groundwater Sampling					
Sampling Location ID Number [1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples** (identify field duplicates)[2]	**SOP Reference** [3]
ST012-U11	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1 + 1 field duplicate	SOP 10D
ST012-W11	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-W30	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-W34	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-W36	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D

Table 18.1 – Baseline Groundwater Sampling					
Sampling Location ID Number [1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples** (identify field duplicates)[2]	**SOP Reference** [3]
ST012-W37	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-CZ12	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-CZ14	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-CZ16	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-UWBZ21	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-UWBZ23	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-CZ18	VOCs ICP Metals	GW	EPA 8260B SPE 8270C	1	SOP 10D

Table 18.1 – Baseline Groundwater Sampling					
Sampling Location ID Number [1]	Analytical Groups or Field Tests	Matrix	Method	Number of Samples (identify field duplicates)[2]	SOP Reference [3]
	Sulfate and Nitrate Alkalinity Sulfate field screening		EPA 6010C EPA 9056A SM 2320B		
ST012-CZ19	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-UWBZ10	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-UWBZ22	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-UWBZ26	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-UWBZ27	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ17	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A	1 + 1 field duplicate	SOP 10D

Table 18.1 – Baseline Groundwater Sampling					
Sampling Location ID Number [1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples** (identify field duplicates)[2]	**SOP Reference** [3]
	Sulfate field screening		SM 2320B		
ST012-LSZ28	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ18	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ29	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ14	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ26	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ12	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D

Table 18.1 – Baseline Groundwater Sampling					
Sampling Location ID Number [1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples** (identify field duplicates)[2]	**SOP Reference** [3]
ST012-LSZ36	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ11	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1 + 1 field duplicate	SOP 10D
ST012-LSZ35	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ39	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ23	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ38	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ09	VOCs ICP Metals	GW	EPA 8260B SPE 8270C	1	SOP 10D

Table 18.1 – Baseline Groundwater Sampling					
Sampling Location ID Number [1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples** (identify field duplicates)[2]	**SOP Reference** [3]
	Sulfate and Nitrate Alkalinity Sulfate field screening		EPA 6010C EPA 9056A SM 2320B		
ST012-LSZ37	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-CZ21-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-CZ22-EBR / UWBZ35-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	2	SOP 10D
ST012-UWBZ28-EBR / LSZ51-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	2	SOP 10D
ST012-UWBZ29-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1 + 1 field duplicate	SOP 10D
ST012-UWBZ30-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A	1	SOP 10D

Table 18.1 – Baseline Groundwater Sampling					
Sampling Location ID Number [1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples** (identify field duplicates)[2]	**SOP Reference** [3]
	Sulfate field screening		SM 2320B		
ST012-UWBZ31-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-UWBZ32-EBR / LSZ47-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	2	SOP 10D
ST012-UWBZ33-EBR / LSZ48-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	2	SOP 10D
ST012-UWBZ34-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-UWBZ36-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1 + 1 field duplicate	SOP 10D
ST012-LSZ43-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D

Table 18.1 – Baseline Groundwater Sampling					
Sampling Location ID Number [1]	Analytical Groups or Field Tests	Matrix	Method	Number of Samples (identify field duplicates)[2]	SOP Reference [3]
ST012-LSZ44-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ45-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ46-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ49-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ50-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity Sulfate field screening	GW	EPA 8260B SPE 8270C EPA 6010C EPA 9056A SM 2320B	1 + 1 field duplicate	SOP 10D

Notes:
EPA – United States Environmental Protection Agency
GW – groundwater
ICP – inductively coupled plasma
ID – identification
SM – Standard Method
SOP – Standard Operating Procedure
SVOCs – semi-volatile organic compounds
VOCs – volatile organic compound
[1] Well locations are provided in Figure 3-1.
[2] Field duplicates may be collected from another well based on field conditions at the time of the sampling event.
[3] SOPs for groundwater well sampling are discussed above in Worksheet #14 and #21.

Table 18.2 – Quarterly Injection Well/Monthly Injection Solution Sampling					
Sampling Location ID Number[1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples** (identify field duplicates)[2]	**SOP Reference**[3]
TEA Injection Solution, grab sample	ICP Metals Sulfate	GW	EPA 6010C EPA 9056A	3 (monthly)	NA
ST012-U11	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1 + 1 field duplicate	SOP 10D
ST012-W11	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-W30	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-W34	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-W36	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-W37	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-CZ12	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-CZ14	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-CZ16	VOCs	GW	EPA 8260B	1	SOP 10D

Table 18.2 – Quarterly Injection Well/Monthly Injection Solution Sampling					
Sampling Location ID Number [1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples** (identify field duplicates)[2]	**SOP Reference** [3]
	ICP Metals Sulfate and Nitrate Alkalinity		EPA 6010C EPA 9056A SM 2320B		
ST012-UWBZ21	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-UWBZ23	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-CZ2-EBR / UWBZ35-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	2	SOP 10D
ST012-UWBZ28-EBR / LSZ51-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	2	SOP 10D
ST012-UWBZ29-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-UWBZ32-EBR / LSZ47-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	2	SOP 10D
ST012-UWBZ33-EBR / LSZ48-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	2	SOP 10D
ST012-UWBZ34-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D

Table 18.2 – Quarterly Injection Well/Monthly Injection Solution Sampling					
Sampling Location ID Number [1]	Analytical Groups or Field Tests	Matrix	Method	Number of Samples (identify field duplicates)[2]	SOP Reference [3]
ST012-UWBZ36-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ43-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ44-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ45-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ46-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D
ST012-LSZ49-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1 + 1 field duplicate	SOP 10D
ST012-LSZ50-EBR	VOCs ICP Metals Sulfate and Nitrate Alkalinity	GW	EPA 8260B EPA 6010C EPA 9056A SM 2320B	1	SOP 10D

Notes:
EPA – United States Environmental Protection Agency
GW – groundwater
ICP – inductively coupled plasma
ID – identification
SM – Standard Method
SOP – Standard Operating Procedure
VOCs – volatile organic compound
[1] Well locations are provided in Figure 3-1.
[2] Field duplicates may be collected from another well based on field conditions at the time of the sampling event.
[3] SOPs for groundwater well sampling are discussed above in Worksheet #14 and #21.

Table 18.3 – Quarterly Extraction Well Sampling					
Sampling Location ID Number [1]	Analytical Groups or Field Tests	Matrix	Method	Number of Samples (identify field duplicates)[2]	SOP Reference [3]
ST012-CZ21-EBR	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-UWBZ30-EBR	VOCs	GW	EPA 8260B	1 + 1 duplicate	NA, grab sample
ST012-UWBZ31-EBR	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-CZ18	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-CZ19	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-UWBZ10	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-UWBZ22	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-UWBZ26	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-UWBZ27	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ17	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ28	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ18	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ29	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ14	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ26	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ12	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ36	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ11	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ35	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ39	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ23	VOCs	GW	EPA 8260B	1	NA, grab sample

Table 18.3 – Quarterly Extraction Well Sampling					
Sampling Location ID Number [1]	Analytical Groups or Field Tests	Matrix	Method	Number of Samples (identify field duplicates)[2]	SOP Reference [3]
ST012-LSZ38	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ09	VOCs	GW	EPA 8260B	1	NA, grab sample
ST012-LSZ37	VOCs	GW	EPA 8260B	1	NA, grab sample

Notes:
EPA – United States Environmental Protection Agency
GW – groundwater
ID – identification
NA – not available
SOP – Standard Operating Procedure
VOCs – volatile organic compound
[1] Well locations are provided in Figure 3-1.
[2] Field duplicates may be collected from another well based on field conditions at the time of the sampling event.
[3] SOPs for groundwater well sampling are discussed above in Worksheet #14 and #21.

Table 18.4 – Semiannual Extraction Well Sampling					
Sampling Location ID Number [1]	Analytical Groups or Field Tests	Matrix	Method	Number of Samples (identify field duplicates)[2]	SOP Reference [3]
ST012-CZ21-EBR	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-UWBZ30-EBR	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-UWBZ31-EBR	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-CZ18	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1+1 duplicate	NA, grab sample
ST012-CZ19	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-UWBZ10	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-UWBZ22	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-UWBZ26	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-UWBZ27	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ17	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample

Table 18.4 – Semiannual Extraction Well Sampling					
Sampling Location ID Number [1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples** (identify field duplicates)[2]	**SOP Reference** [3]
ST012-LSZ28	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ18	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ29	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ14	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ26	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ12	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ36	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ11	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ35	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ39	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ23	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ38	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ09	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample
ST012-LSZ37	TPH ICP Metals	GW	EPA 8015B EPA 6010C	1	NA, grab sample

Notes:
EPA – United States Environmental Protection Agency
GW – groundwater
ICP – inductively coupled plasma
ID – identification
NA – not available
SOP – Standard Operating Procedure
TPH – total petroleum hydrocarbons
[1] Well locations are provided in Figure 3-1.
[2] Field duplicates may be collected from another well based on field conditions at the time of the sampling event.
[3] SOPs for groundwater well sampling are discussed above in Worksheet #14 and #21.

Table 18.5 – Biweekly to Monthly Extraction Well Sampling					
Sampling Location ID Number [1]	Analytical Groups or Field Tests	Matrix	Method	Number of Samples (identify field duplicates)[2]	SOP Reference [3]
ST012-UWBZ30-EBR	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-UWBZ10	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-UWBZ22	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-UWBZ26	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-UWBZ27	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ17	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ28	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ18	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ29	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ14	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ26	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ12	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly	NA, grab sample

Table 18.5 – Biweekly to Monthly Extraction Well Sampling					
Sampling Location ID Number[1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples (identify field duplicates)[2]**	**SOP Reference[3]**
				• 9056A for every 10% of field screening samples	
ST012-LSZ36	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ11	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ35	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ23	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ38	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ09	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ37	Sulfate	GW	EPA 9056A Sulfate field screening	• Biweekly for first month, monthly • 9056A for every 10% of field screening samples	NA, grab sample

Notes:
EPA – United States Environmental Protection Agency
GW – groundwater
ID – identification
NA – not available
SOP – Standard Operating Procedure
[1] Well locations are provided in Figure 3-1.
[2] Field duplicates may be collected from another well based on field conditions at the time of the sampling event.
[3] SOPs for groundwater well sampling are discussed above in Worksheet #14 and #21.

Table 18.6 – Weekly to Monthly Extraction Well Sampling					
Sampling Location ID Number [1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples** (identify field duplicates)[2]	**SOP Reference [3]**
ST012-CZ18	Sulfate	GW	EPA 9056A Sulfate field screening	• Weekly for two months, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-CZ19	Sulfate	GW	EPA 9056A Sulfate field screening	• Weekly for two months, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-CZ21-EBR	Sulfate	GW	EPA 9056A Sulfate field screening	• Weekly for two months, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-UWBZ31-EBR	Sulfate	GW	EPA 9056A Sulfate field screening	• Weekly for two months, monthly • 9056A for every 10% of field screening samples	NA, grab sample
ST012-LSZ39	Sulfate	GW	EPA 9056A Sulfate field screening	• Weekly for two months, monthly • 9056A for every 10% of field screening samples	NA, grab sample

Notes:
EPA – United States Environmental Protection Agency
GW – groundwater
ID – identification
NA – not available
SOP – Standard Operating Procedured
[1] Well locations are provided in Figure 3-1.
[2] Field duplicates may be collected from another well based on field conditions at the time of the sampling event.
[3] SOPs for groundwater well sampling are discussed above in Worksheet #14 and #21.

Table 18.7 – Quarterly Monitoring Well Sampling					
Sampling Location ID Number [1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples** (identify field duplicates)[2]	**SOP Reference [3]**
ST012-C02	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1 + 1 duplicate	SOP 10D
ST012-U02	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1	SOP 10D
ST012-W12	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1	SOP 10D
ST012-U37	VOCs ICP Metals	GW	EPA 8260B EPA 6010C	1	SOP 10D

Table 18.7 – Quarterly Monitoring Well Sampling					
Sampling Location ID Number [1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples** (identify field duplicates)[2]	**SOP Reference** [3]
	Sulfate		EPA 9056A		
ST012-RB-3A	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1	SOP 10D
ST012-W24	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1	SOP 10D
ST012-U38	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1	SOP 10D
ST012-W38	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1	SOP 10D
ST012-U12	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1	SOP 10D
ST012-CZ01	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1	SOP 10D
ST012-CZ05	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1	SOP 10D
ST012-UWBZ19	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1	SOP 10D
ST012-UWBZ24	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1	SOP 10D
ST012-LSZ21	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1	SOP 10D
ST012-LSZ27	VOCs ICP Metals Sulfate	GW	EPA 8260B EPA 6010C EPA 9056A	1	SOP 10D

Notes:
EPA – United States Environmental Protection Agency
GW – groundwater
ICP – inductively coupled plasma
ID – identification
SOP – Standard Operating Procedure
VOCs – volatile organic compound
[1] Well locations are provided in Figure 3-1.
[2] Field duplicates may be collected from another well based on field conditions at the time of the sampling event.
[3] SOPs for groundwater well sampling are discussed above in Worksheet #14 and #21.

Table 18.8 – Process Water Sampling					
Sampling Location ID Number[1]	**Analytical Groups or Field Tests**	**Matrix**	**Method**	**Number of Samples** (identify field duplicates)[2]	**SOP Reference**[3]
Treatment System Influent	VOCs	GW	EPA 8260B	Monthly	NA, grab sample
GAC Influent	VOCs SVOCs Pesticides/PCBs	GW	EPA 8260B EPA 8270C EPA 8081/8082	Weekly until concentrations stabilize, monthly thereafter	NA, grab sample
GAC Midfluent	VOCs SVOCs Pesticides/PCBs	GW	EPA 8260B EPA 8270C EPA 8081/8082[4]	Weekly until concentrations stabilize, monthly thereafter	NA, grab sample
GAC Effluent	VOCs SVOCs Pesticides/PCBs	GW	EPA 8260B EPA 8270C EPA 8081/8082[4]	Quarterly	10D

Notes:
EPA – United States Environmental Protection Agency
GW – groundwater
ID – identification
PCBs – polychlorinated biphenyls
SOP – Standard Operating Procedure
SVOCs – semi-volatile organic compounds
VOCs – volatile organic compound
[1] Well locations are provided in Figure 3-1.
[2] Field duplicates may be collected from another well based on field conditions at the time of the sampling event.
[3] SOPs for groundwater well sampling are discussed above in Worksheet #14 and #21.
[4] A second sample sent for HRGC/HRMS analysis if there are any detections of prohibited compounds.

QAPP WORKSHEET NO. 19 – ANALYTICAL SOP REQUIREMENTS TABLE

The table below summarizes the analytical SOP requirements for the analytical parameters that are anticipated at for the field test at ST012.

Analytical Parameter	Analytical Method	Matrix	Holding Time (from sample date)	Preservation
Volatile organic compounds	8260B	Water	14 days	HCl, pH < 2, zero headspace and 4°C
Semi-volatile organic compounds	8270C	Water	14 days	HCl, pH < 2, zero headspace and 4°C
Total petroleum hydrocarbons (DRO/GRO)	8015B	Water	Extract within 14 days; analyze within 40 days (DRO); analyze within 14 days (GRO)	4°C (DRO); HCl pH<2 and 4°C (GRO)
Pesticides/PCBs	8081/8082	Water		
Anions (Ion Chromatography)	9056A	Water	28 days for Sulfate; 48 hours for Nitrate	4 °C
ICP Metals	6010B	Water	Analyze within 180 days; analyze within 28 days if Hg included	HNO_3, pH <2; 4°C
HRGC/HRMS Pesticides	1699	Water	7 days	4 °C +/- 2 °C
qPCR	qPCR	Water	24-48 hours	4 °C
PLFA	PLFA	Water	24-48 hours	4 °C

Notes:
°C - Degrees Celsius
DRO – Diesel Range Organics
GRO – Gasoline Range Organics
ICP - inductively coupled plasma
PLFA – phospholipid fatty acid
qPCR - quantitative polymerase chain reaction
[1] TestAmerica proposed a new SOP for EPA Methods 8081/8082. The new SOP is provided as Attachment B.

QAPP WORKSHEET NO. 20 – FIELD QUALITY CONTROL SAMPLE SUMMARY TABLES

Groundwater sampling activities will follow the QA/QC procedures presented in this UFP QAPP. Results of calibration samples, blank samples, LCSs, surrogates, internal standards, MS/MSD samples, and duplicates will be compared to the acceptance criteria specified in this UFP QAPP to determine if data are usable to meet the investigation objectives.

The QC sampling criteria for samples collected at site ST012 are provided in the following tables and QAPP Worksheet No. 20, Field Quality Control Summary Table. Sampling handling and labeling procedures shall be conducted per SOP No. 15, *Sample Handling* .

Analytical Parameter	No. of Field Duplicate Pairs	Organic		Inorganic		No. of Trip Blanks	No. of Equip. Blanks (1)
		No. of MS	No. of MSD	No. of MS	No. of Duplicates		
All Parameters tested by TestAmerica	10 %	5 %	5 %	5 %	5 %	1 per cooler containing VOCs	5 %

Notes:
% = percent
No. = number
MS = matrix spike
MSD = matrix spike duplicate
Equip. = equipment
VOCs = volatile organic compounds
(1) Equipment blanks will be collected at a frequency of 5 percent (1:20) per equipment type.

Method	Quality Control Check	Minimum Frequency
PLFA	Initial Assay Calibration (standard curve)	Once per assay
	Continuing Calibration Verification	10% frequency and at the end of the analytical batch
	Method Blank	One per analytical batch
	Laboratory Control Sample	One per analytical batch
	Field duplicate	5%
qPCR	Assay Calibration (Standard Curve)	Primary – initial
	Laboratory (sample) Duplicate	All field samples
	Field duplicate	5%
	Assay Negative Control (Blank)	1 per analytical assay plate in duplicate
	DNA extraction negative control	1 per analytical batch
	Positive Control	1 per analytical assay plate in duplicate

Notes:
PLFA – Phospholipid Fatty Acid, qPCR – quantitative polymerase chain reaction

QAPP WORKSHEET NO. 21 – PROJECT SAMPLING SOP REFERENCES TABLE

Reference Number	Title, Revision Date and/or Number	Originating Organization	Equipment Type	Modified for Project Work? (Yes or No)	Comments
SOP-1	Equipment Decontamination	Amec Foster Wheeler	Decontamination fluids, equipment, buckets, brushes, sprayers, towels	Yes ☐ No ☒	
SOP-2	Documentation of Field Activities	Amec Foster Wheeler	Field forms	Yes ☐ No ☒	
SOP-10B	Subsurface Soil Sampling	Amec Foster Wheeler	As described in SOP-10B	Yes ☐ No ☒	
SOP-10D	Low-Flow Sampling	Amec Foster Wheeler	As described in SOP-10D	Yes ☐ No ☒	
SOP-15	Sample Handling	Amec Foster Wheeler	As described in SOP-15	Yes ☐ No ☒	
SOP-16	Investigation-Derived Waste Management	Amec Foster Wheeler	As described in SOP-16	Yes ☐ No ☒	

Notes:
SOP – standard operating procedure

QAPP WORKSHEET NO. 23 – ANALYTICAL LABORATORY SOP REFERENCES TABLE

The investigation and remediation activities will involve the analysis of samples collected from groundwater and injection solutions. Based on available historical data generated at the site, samples may be analyzed for chemical and/or waste characterization parameters. Worksheet No. 30 presents the anticipated analytical services program. Laboratory methods used at this site for the purposes proposed will be consistent with EPA methods and QA/QC procedures and the DoD QSM Version 4.2 (DoD, 2010). At a minimum, the analytical laboratory will be required to maintain a QA program and SOPs that is consistent with the DoD QSM, National Environmental Laboratory Accreditation Program (NELAP), and EPA requirements.

Fixed Laboratory Analytical Methods and SOPs for TestAmerica

The samples collected during the progress of the Performance Based Remediation will be submitted to the TestAmerica Denver, Colorado laboratory. Attachment D provides a written description of the TestAmerica Denver, Colorado laboratory QA Program and summary of all active laboratory SOPs. SOPs for each analytical method are available upon request. The TestAmerica Denver, Colorado laboratory is certified by the Arizona Department of Health Services, license number AZ0713.

Laboratories providing services will be accredited under the NELAP and certified for Clean Water Act and Resource Conservation and Recovery Act analyses. Analyses will be completed for most parameters using the current version of *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (EPA, 2008, Final Updated IV Edition and subsequent updates) and EPA analytical methods (EPA Forum on Environmental Measurements website).

The analytical methods and laboratory quantitation limit (QL) and MDLs necessary are defined in Worksheet #15. Analyses will be conducted by the laboratory so that the task-specific requirements are met. Additional evaluation of QL needs may be necessary during the course of the investigation and remediation activities. Any modifications to analytical data and data reporting will be specified as necessary.

The principal contacts are the Program Managers for AFCEC and Amec Foster Wheeler. The Amec Foster Wheeler Program Chemist will coordinate with the appointed Laboratory PM.

Fixed Laboratory Analytical Methods and SOPs for Microbial Insights

Microbial Insights will be used for all biological fixed laboratory analyses, if necessary. They provide specialty molecular based biology analyses to assess microbial populations, and there are no certifications or accreditations available for this type of testing. All SOPs for Microbial Insights laboratory analyses contain proprietary information and are not distributed outside the laboratory.

Analytical Methods

The analytical program is applicable to ST012. A listing of analytical methods for groundwater sampling that will be used during the field test activities are presented in Worksheet No. 30.

QAPP WORKSHEET NO. 30 – ANALYTICAL SERVICES TABLE

Analytical Parameter (all for water)	Analytical Method[1]
Volatile organic compounds	8260B
Semi-volatile organic compounds	8270C
Total petroleum hydrocarbons (DRO/GRO)	8015B
Pesticides - HRGC/HRMS	1699[2]
Pesticides/PCBs	8081/8082[3]
Anions (Ion Chromatography)	9056A
ICP Metals	6010B
qPCR	qPCR
PLFA	PLFA

Notes:
DRO – diesel range organics
GRO – gasoline range organics
HRGC/HRMS – high resolution gas chromatography/high resolution mass spectrometry
ICP – inductively coupled plasma
PCBs – polychlorinated biphenyls
PLFA – phospholipid fatty acid
qPCR – quantitative polymerase chain reaction
[1] The most recent version of the proposed method will be used
[2] TestAmerica SOPs for this methods was not included in the Program QAPP and is provided in Attachment B.
[3] The proposed new TestAmerica SOP for EPA Method 8081/8082 is provided in Attachment B.

ATTACHMENT B

TestAmerica SOPs: Method 1699 and Methods 8081/8082

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Title: Chlorinated Pesticides [Method No. 8081A & 8081B]

Approvals (Signature/Date):

7-29-15		30 July 15	
Dennis Jonsrud Technical Specialist	Date	Adam Alban Health & Safety Manager / Coordinator	Date
7/30/15		7/30/15	
Margaret S. Sleevi Quality Assurance Manager	Date	William S. Cicero Laboratory Director	Date

Facility Distribution No. ___________ **Distributed To:**___________________

1.0 Scope and Application

1.1 This standard operating procedure (SOP) describes the determination of chlorinated pesticides using the methodology described in EPA SW-846 Method 8081A and 8081B with 8000B or 8000C as specified by project requirements.

1.2 This SOP is applicable to the gas chromatographic (GC) analysis of extracts of soil and water samples. Table 1 lists the compounds that can be determined by this method and their associated routine reporting limits (RLs).

1.3 This SOP does not include the procedures for extracting soil and water samples. Refer to the following SOPs for sample extraction procedures:

DV-OP-0006	Extraction of Aqueous Samples by Separatory Funnel, SW-846 3510C
DV-OP-0007	Concentration of Organic Extracts, SW-846 3510C, 3520C, 3540C, and 3550C
DV-OP-0016 DV-OP-0015	Ultrasonic Extraction of Solid Samples by SW-846 3550C Microwave Extraction of Solid Samples by SW-846 3546

1.4 Analytes, Matrix(s), and Reporting Limits

See Table 1 for analytes and reporting limits by matrix.

1.5 This SOP contains a Large Volume Injection (LVI) procedure. This procedure has not been approved by the State of South Carolina and therefore no samples from South Carolina may be analyzed using LVI.

2.0 Summary of Method

2.1 Sample Preparation

2.1.1 Chlorinated pesticides are extracted from a one-liter water sample with methylene chloride using a separatory funnel (Method 3510C). Detailed instructions are given in SOP DV-OP-0006. The methylene chloride extract is exchanged to hexane as described in SOP DV-OP-0007. An alternate procedure has been developed using a lower volume of sample (250 mL to a final volume of 5 mL) and a larger injection volume in order to minimize shipping requirements and conserve the reagents needed for extraction.

2.1.2 Chlorinated pesticides are extracted from a 30-gram soil subsample into a 50:50 acetone-methylene chloride solution by sonication (Method 3550C) or by microwave extraction (Method 3546). The extract is dried and exchanged to hexane. Detailed instructions are given in SOPs DV-OP-0016 and DV-OP-0015.

2.1.3 SOP DV-OP-0007 provides instructions for the concentration and cleanup of sample extracts. Florisil is used to clean extracts that show color or when requested in order to minimize interferences when they are observed from the analysis. Sulfur is removed if observed. All extracts are in hexane and the final extract volume is 10 mL. For the LVI method the final extract volume is 5 mL.

2.2 Analysis

2.2.1 Samples are analyzed using a gas chromatograph equipped with dual columns and dual electron capture detectors (ECDs).

2.2.2 The instrument is calibrated using internal standards. Compounds are identified by their retention time on the columns.

2.2.3 Positive results from the primary column are confirmed with a second, dissimilar column. The laboratory maintains a total of four dissimilar columns for additional confirmation capability.

3.0 Definitions

3.1 Single-Component Pesticides: A pesticide formulation that consists of a single chemical compound. Most of the analytes determined by this procedure are single-compound pesticides.

3.2 Multi-Component Pesticides: A pesticide formulation that consists of more than one chemical compound. Toxaphene and Technical Chlordane are production mixtures of multiple compounds. Toxaphene is manufactured by the chlorination of camphenes, which produces a variety of compounds, not all of which are chromatographically resolved. Technical Chlordane is produced by the chlorination of a mixture of camphenes and pinenes.

3.3 Chlordane: As just described, Technical Chlordane (CAS# 12789-03-6) is a mixture of compounds. Method 8081A, Section 7.6.2 and Method 8081B, Section 11.6.2 note that Technical Chlordane includes at least 11 major components and 30 minor components, and adds "the exact percentage of each [*cis*-chlordane and *trans*-chlordane] in the technical material is not completely defined, and is not consistent from batch to batch." The laboratory has found that manufacturing lots of Technical Chlordane produced at different times or at different production facilities have different ratios of the key components. For this reason, it is more common to analyze for the major components of technical Chlordane (α-Chlordane, γ-Chlordane, and heptachlor) instead of analyzing for the total mixture. For the purpose of reporting results under this SOP, the following compounds are reported. Alpha-chlordane (*cis*-chlordane) CAS # 5103-71-9 and gamma-chlordane (*trans*-chlordane) CAS # 5103-74-2. trans-Chlordane has also been identified as beta-chlordane. The laboratory may also report chlordane (not otherwise specified) or, n.o.s under CAS# 57-74-9.

3.4 The quality control terms used in this procedure are consistent with SW-846 terminology. Definitions are provided in the glossary of the TestAmerica Denver Quality Assurance Manual (QAM) and SOP DV-QA-003P.

4.0 Interferences

4.1 Contamination by carryover can occur when a low concentration sample is analyzed immediately following a high concentration sample. It is the laboratory's policy to reanalyze any samples that follow an unusually concentrated sample (well above the high level calibration standard) and that show detectable levels of the same compounds that appeared in the preceding concentrated sample.

4.2 Interferences in the GC analysis arise from many compounds amenable to gas chromatography that give a measurable response on the electron capture detector. Phthalate esters, which are common plasticizers, can pose a major problem in the determinations. Interferences from phthalates are minimized by avoiding contact with any plastic materials.

4.3 Sulfur will interfere, and, when observed, is removed using cleanup procedures described in SOP DV-OP-0007. An NCM which indicates the lot number of the materials used for cleanup is provided whenever a cleanup procedure is used.

4.4 Soil and water sample extracts are subject to Florisil cleanup when the extracts have noticeable color or whenever there is clear evidence of interferences in the initial sample chromatograms. Florisil removes low- to medium-molecular weight polar organic interferences from sample extracts. One limitation for this cleanup method is that recoveries for the most polar compounds, endosulfan sulfate and endrin aldehyde in particular, will be lower. Florisil has been observed to remove the compound kepone and is not used where the determination of kepone is required. Instructions for performing Florisil cleanups can be found in SOP DV-OP-0007. An NCM which indicates the lot number of the materials used for cleanup is provided whenever a cleanup procedure is used.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 Eye protection that satisfies ANSI Z87.1, laboratory coat, and nitrile gloves must be worn while handling samples, standards, solvents, and reagents. Disposable gloves that have been contaminated must be removed and discarded; non-disposable gloves must be cleaned immediately.

5.1.2 The gas chromatograph contains zones that have elevated temperatures. The analyst needs to be aware of the locations of those zones, and must cool them to room temperature prior to working on them.

5.1.3 There are areas of high voltage in the gas chromatograph. Depending on the type of work involved, either turn the power to the instrument off, or disconnect it from its source of power.

5.1.4 The ECD contains a ^{63}Ni radioactive source. All ^{63}Ni sources shall be leak tested every six months, or in accordance with the facility's radioactive material license. All ^{63}Ni sources shall be inventoried every six months. If a detector is missing, the Radiation Safety Officer shall be immediately notified and a letter sent to the Colorado Department of Public Health and Environment. Follow the proper procedures and precautions for the safe handling of radioactive materials when handling the ECDs in the event that leakage may have occurred.

5.1.5 As a safety precaution, all standards, samples, and extracts are handled in an approved fume hood.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Material	Hazards	Exposure Limit (1)	Signs and Symptoms of Exposure
Acetone	Flammable	1000 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Hexane	Flammable Irritant	500 ppm (TWA)	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.
Methanol	Flammable Poison Irritant	200 ppm (TWA)	A slight irritant to the mucous membranes. Toxic effects are exerted upon nervous system, particularly the optic nerve. Symptoms of overexposure may include headache, drowsiness, and dizziness. Methyl alcohol is a defatting agent and may cause skin to become dry and cracked. Skin absorption can occur; symptoms may parallel inhalation exposure. Irritant to the eyes.
(1) Exposure limit refers to the OSHA regulatory exposure limit.			

6.0 Equipment and Supplies

6.1 An analytical system complete with a gas chromatograph and dual ECD (Ni-63) detectors is required. A data system capable of measuring peak area and/or height is required. The instruments typically used for this method are HP 6890 instrument C and HP 6890N for instruments P1 and P2.

6.2 An analytical balance capable of weighing to 0.01 g.

6.3 Computer Software and Hardware

Please refer to the master list of documents and software located on R:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

6.4 Columns

6.4.1 Primary Column: CLPI, 30 m X 0.32 mm id (used in instruments P1 and P2).

6.4.2 Secondary Column: CLPII, 30 m X 0.32 mm id (used in instruments P1 and P2).

6.4.3 Additional columns that can be used for confirmation include 30 m X 0.32 mm id RxiSil 35-MS or Rxi-XLB (used in instrument C).

6.5 Autosampler vials, crimp-top cap with PTFE-faced septa

6.6 Siltek Y-splitter, thermogreen septa, Siltek guard columns, ferrules, deactivated injection port liners (Agilent Ultra Inert, Siltek, or Sky liners all work well), Siltek glass wool, gold plated seals.

6.7 Microsyringes, various sizes, for standards preparation, sample injection, and extract dilution.

6.8 Class A volumetric flasks various sizes.

7.0 Reagents and Standards

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1 Reagents

7.1.1 Hexane, pesticide grade; each lot tested for purity prior to use per SOP CA-Q-S-001.

7.1.2 Carrier gas, ≥ 99.99999% pure hydrogen or helium

7.1.3 Make-up gas, ≥ 99.99980% pure nitrogen

7.2 Standards Verification

All standards are subject to verification using a second-source standard before they are used for sample analysis. This process is described in SOP DV-QA-0015.

7.3 Storage of Stock Standards

7.3.1 Standards are purchased from commercial vendors and are received as certified solutions in flame sealed ampoules. Neat stocks with applicable certification may also be used. Stock standards are stored refrigerated at ≤ 6 °C. All stock standards must be protected from light. Stock standard solutions should be brought to room temperature before using.

7.3.2 Dilutions from stock standards cannot have a later expiration date than the date assigned to the parent stock solutions. Stock standards are monitored for signs of degradation or evaporation. The standards must be replaced at least every six months or sooner if comparison with check standards indicates a problem. Kepone in particular may demonstrate signs of degradation faster than the other compounds, and/or the expiration date. Endosulfan I and II appear to degrade in the presence of methanol. gamma-BHC appears to degrade in the presence of acetone.

7.4 Calibration Stock Standards

NOTE: The availability of the specific commercial standard solutions upon which the following sections are based may change at any time. As a result, it may be necessary to alter the dilution scheme presented herein to accommodate changes in stock standard concentrations. All such changes are documented in the standards preparation records.

7.4.1 Routine Pesticide AB Mix Stock Standard, 2,000 µg/mL

The routine pesticide AB mix stock standard (**8081ABResPS**), Restek 32415, contains all of the “routine” single-component pesticides, as identified in Table 1 with the addition of Hexachlorobenzene at 100 µg/mL (**8081HCBStkPS**) (Accustandard APP-9-112), Mirex at 100 µg/mL (**8081MirxStkPS**)(Accustandard P-066S) and Isodrin at 1000 µg/mL (**8081IsodrinPS**) (Accustandard P471S-10x).

7.4.2 Surrogate B Mix Stock Standard, 200 µg/mL

The surrogate B mix stock standard (**AR_SURR_RES**) (Restek 32000) contains decachlorobiphenyl (DCB) and tetrachloro-*m*-xylene (TCMX).

7.4.3 Toxaphene Stock, 5000 µg/mL

The Toxaphene stock standard (**8081ToxPS**) (Restek 32071) contains a specific production mixture of Toxaphene. This mixture does not necessarily match all possible production mixtures that could be found in the environment. This can present problems for Toxaphene quantitation (see Section 12).

7.4.4 Chlordane Stock, 5000 µg/mL

The Chlordane stock (**8081ChlrStkPS**) (Restek 32072) contains Technical Chlordane (CAS# 12789-03-6).

7.4.5 Appendix IX Calibration Stock

The Appendix IX stock calibration mixture (**8081AP9StkPS**) (Accustandard S-6880 custom) contains the compounds at the concentrations listed in the following table. Propachlor at 1000 ug/mL is also added to the mixture (Accustandard P-215S-10x).

Appendix IX Calibration Stock Standard

Compound	Concentration (µg/mL)
2,4'-DDD	100
2,4'-DDE	100
2,4'-DDT	100
Chlorobenzilate	1,000
Chlorpyrifos	500
Diallate	10,000
Dicofol	1,000
Kepone	1,000
DBPP	5,000

7.4.6 Internal Standard stock

A commercially prepared stock standard solution is obtained that contains the internal standard 1-bromo-2-nitrobenzene in acetone, at a concentration of 1000 µg/mL. The current vendor is RESTEK catalog #32279, other vendors may be used.

7.4.7 Non-Routine Compounds

Other, non-routine compounds not listed in this section may be requested by a client and may be added to this procedure.

7.4.7.1 In these cases, all stock solutions will be obtained from commercial sources and will be verified with a second-source standard as described in Section 7.2 above.

7.4.7.2 Non-routine standards will be stored and treated as described in Section 7.3 above or as specified by the manufacturer.

7.4.7.3 Subsequent dilutions of specially requested compounds will be determined in a manner consistent with the client's recommendations for number of calibration points, inclusion of reporting limit, and concentration range adequate to represent the linearity of the instrument.

7.4.7.4 These specially requested, non-routine compounds either may be added to the dilution scheme used for routine compounds or may be prepared as a separate calibration.

7.4.7.5 All standards preparation for non-routine compounds shall be documented using the same method that is used for routine compounds.

7.5 Intermediate Level Calibration Standards

7.5.1 Routine Pesticide Mix C Intermediate Calibration Standard, 1.0 µg/mL (**8081ABCalStk**). The intermediate level calibration standard for routine pesticide compounds including Hexachlorobenzene and Mirex is prepared by diluting the AB (Section 7.4.1) and B (Section 7.4.2) mix stock standards in hexane to 100 mL final volume as follows (all compounds are the same final concentration):

Mix C Intermediate Calibration Standard

Stock AB mix (mL)	Stock B (mL)	Mirex & HCB (mL)	Isodrin (mL)	Final Concentration of Each Pesticide (µg/mL)
0.05	0.5	1.0	0.1	1.0

7.5.2 Appendix IX Intermediate Calibration Standard

The Appendix IX intermediate level calibration standard (**8081AP9CalStk**) is prepared by diluting 0.5 mL of the Appendix IX stock standard (Section 7.4.5) and 0.5 mL of propachlor stock with hexane to a final volume of 50 mL, which results in the following concentrations:

Appendix IX Intermediate Calibration Standard

Compound	Concentration (µg/mL)
2,4'-DDD	1.0
2,4'-DDE	1.0
2,4'-DDT	1.0
Chlorobenzilate	10.
Chlorpyrifos	5.0
DBPP	50.
Diallate	100.
Propachlor	10.
Dicofol	10.
Kepone	10.

7.6 Working Level Calibration Standards

7.6.1 Routine Pesticide AB Mix Working Level Calibration Standards

The following volumes of the 1.0 µg/mL Mix C intermediate standard (Section 7.5.1) are diluted to 100 mL with hexane to produce calibration standards at 6 concentration levels, as summarized in the following table:

AB Mix Working Level Calibration Standards

Level	Volume of Mix C Intermediate Std (mL)	Final Concentration (µg/mL)
1 (**8081IcalL1**)	0.4	0.0040
2 (**8081IcalL2**)	1.0	0.010
3 (**8081IcalL3**)	2.5	0.025
4* (**8081IcalL4**)	5.0	0.050
5 (**8081IcalL5**)	7.5	0.075
6 (**8081IcalL6**)	10	0.10

* *This level is used as the Continuing Calibration Verification (CCV) standard. As a result, it may be convenient to make a larger volume of this calibration level, by diluting 12.5 mL of the intermediate standard with hexane to a final volume of 250 mL.*

7.6.2 Toxaphene Working Level Calibration Standards

The following volumes of the 5000 µg/mL Toxaphene stock standard (Section 7.4.3) are diluted with hexane to the final volumes indicated in the following table:

Toxaphene Working Level Calibration Standards

Level	Volume of Stock Std (mL)	Final Volume (mL)	Final Concentration (µg/mL)
1 (**8081ToxL1**)	0.004	100	0.20
2 (**8081ToxL2**)	0.01	100	0.50
3 (**8081ToxL3**)	0.02	100	1.0
4 (**8081ToxCCVL4**)	0.1	250	2.0
5 (**8081ToxL5**)	0.1	100	5.0
6 (**8081ToxL6**)	0.2	100	10.0

- *Level 4 is used as the CCV standard when running a 5 pt curve.*

7.6.3 Chlordane Working Level Calibration Standards

A chlordane substock (**8081ChlrWSPS**) is prepared by diluting 0.200 mL of the stock described in section 7.4.4 to a final volume of 10 mL with hexane. The following volumes of the resulting 100 µg/mL Chlordane working stock standard are diluted with hexane to the final volume indicated in the following table:

Chlordane Working Level Calibration Standards

Level	Volume of Stock Std (mL)	Final Volume (mL)	Final Concentration (µg/mL)
1 (**8081ChlorL1**)	0.05	100.0	0.05
2 (**8081ChlorL2**)	0.2	100.0	0.20
3 (**8081ChlorL3**)	0.5	100.0	0.50
4* (**8081ChlorL4**)	1.0	100.0	1.0
5 (**8081ChlorL5**)	2.0	100.0	2.0
* *This level is used as the CCV standard.*			

7.6.4 Appendix IX Working Level Calibration Standards

The following volumes of the Appendix IX intermediate calibration standard (Section 7.5.2) are diluted with hexane to a final volume of 1.0 mL. The following table summarizes the final compound concentration ranges for each calibration level. The concentration for each compound at each level is given in Table 3.

Appendix IX Working Level Calibration Standards

Level	Volume of Intermediate Std (mL)	Final Compound Concentration Range (µg/mL)
1	Dilute 1ml Level 2 to 5 ml	0.001 - 0.10
2	0.005	0.005 – 0.50
3	0.010	0.01 - 1.0
4*	0.025	0.025 - 2.5
5	0.035	0.035 - 3.5
6	0.050	0.05 - 5.0
7	0.100	0.1 - 10
* *This level is used as the CCV. Because some compounds in this standard are not stable, it is not recommended to make extra volume of the level 4 standard.*		

7.7 Working Level Calibration Standards for the large volume injection (LVI) procedure

The standards for the LVI method can be prepared using the associated full volume standards described in the previous section 7.6 by mixing equal parts of standard and reagent grade hexane (a 2x dilution) or by simply substituting the appropriate standard from section 7.6 for the corresponding LVI standard that is at the same concentration. Likewise, the LVI standards can be prepared from stock materials. In any case the method of preparation will be completely documented in the standards preparation records. The tables below indicate a typical preparation protocol.

7.7.1 Routine Pesticide AB Mix Working Level LVI Calibration Standards

Calibration standards are prepared by diluting equal volumes of the corresponding calibration standard level from section 7.6.1 with hexane. Calibration standard Level 1 from section 7.6.1 is used to prepare calibration standard Level 1 for the LVI, etc.

AB Mix Working Level LVI Calibration Standards

Level	Volume of Corresponding Std Level (mL) from section 7.6.1 to 2mL final vol.	Final Concentration (µg/mL)
1	1.0	0.002
2	1.0	0.005
3	1.0	0.0125
4*	Use level 3 section 7.6.1	0.025
Level	**Volume of Corresponding Std Level (mL) from section 7.6.1 to 2mL final vol.**	**Final Concentration (µg/mL)**
5	1.0	0.0375
6	Use level 4 section 7.6.1	0.05
* *This level is used as the Continuing Calibration Verification (CCV) standard.*		

7.7.2 Toxaphene Working Level Calibration Standards

Calibration standards for LVI are prepared by diluting equal volumes of the corresponding standard level from section 7.6.2 with reagent hexane.

Toxaphene Working Level Calibration Standards

Level	Volume of Corresponding Std Level (mL) from section 7.6.2	Final Volume (mL)	Final Concentration (µg/mL)
1	1.0	2.0	0.1
2	1.0	2.0	0.25
3	Use Level 2	-	0.5
4	Use Level 3	-	1.0
5	1.0	2.0	2.5
6	Use Level 5	-	5.0
• *Level 4 is used as the CCV standard when running a 5 pt curve.*			

7.7.3 Chlordane Working Level LVI Calibration Standards

Calibration standards for LVI are prepared by diluting equal volumes of the corresponding standard level from section 7.6.3 with reagent hexane.

Chlordane Working Level LVI Calibration Standards

Level	Volume of Corresponding Std Level (mL) from section 7.6.3	Final Volume (mL)	Final Concentration (µg/mL)
1	1.0	2.0	0.025
2	1.0	2.0	0.1
3	1.0	2.0	0.250
4*	Use Level 3	-	0.5
5	Use Level 4	-	1.0
6	Use Level 5	-	2.0
* *This level is used as the CCV standard.*			

7.7.4 Appendix IX Working Level LVI Calibration Standards

Calibration standards for LVI are prepared in the same manner as for the dilution scheme presented in section 7.6.4 by using a 2x dilution of the Appendix IX intermediate calibration standard from section 7.5.2.

Appendix IX Working Level LVI Calibration Standards

Level	Volume of 2x dilution of Intermediate Std (mL)	Final Compound Concentration Range (µg/mL)
1	Dilute 1 ml of level 2 to 5 ml	0.0005 - 0.05
2	0.005	0.0025 – 0.25
3	0.010	0.005 – 0.5
4*	0.025	0.0125 – 1.25
5	0.035	0.0175 – 0.1.75
6	0.050	0.025- 2.5
7	0.100	0.05 - 5
* *This level is used as the CCV. Because some compounds in this standard are not stable, it is not recommended to make extra volume of the level 4 standard.*		

7.8 Second-Source Standards for Initial Calibration Verification (ICV)

The second-source stock standards are purchased from a vendor as different from the one that supplied the stock calibration standards.

7.8.1 Routine Pesticide AB Mix ICV Stock Standard, 2,000 µg/mL, (with Mirex at 100 µg/mL, Isodrin at 5000 ug/mL, HCB at 1000 ug/mL)

Commercial standards containing all single-component pesticide compounds are obtained from a vendor different from the one that supplied the calibration stock standard. The AB mix is prepared from a standard supplied from Restek (**8081ABResSS**) as a separate second source preparation cat # 32415.sec. Typically, the standards are obtained from Ultra Scientific standard EPA-1125 for Hexachlorobenzene (**8081HCBStkSS**), standard PST-720S for Mirex (**8081MirxStkSS**), and standard EPA-1131 for Isodrin (**8081IsodrinSS**).

The current toxaphene second source (**8081ToxSS**) is AccuStandard P-093S-H-10X and it is prepared by diluting 5 µL of the stock standard to 5 mL with hexane.

The current chlordane second source (**8081ChlrStkSS**) is prepared by Restek as a separate second source preparation cat# 32072.sec at a concentration of 5,000 µg/mL. A working substock (**8081ChlSSL3**) is prepared by diluting 0.2 mL of the stock to a final volume of 10 mL with hexane and the working standard is prepared by diluting 5 µL of the working substock standard to 10 mL with hexane.

7.8.2 Appendix IX ICV Stock Standard (8081AP9StkSS)

Commercial standards are obtained at the same concentrations as shown for the calibration stock standards in Section 7.4.5, but from a different vendor (typically Ultra Scientific standard CUS-14331). A second source for propachlor from Ultra PST-865M100A01 at 100 ug/mL is also added to this stock (**8081PropachSS**).

Compound	Concentration (µg/mL)
2,4'-DDD	10
2,4'-DDE	10
2,4'-DDT	10
Chlorobenzilate	100
Chlorpyrifos	50
DBPP	5,000
Diallate	1,000
Dicofol	100
Kepone	100

7.8.3 Surrogate ICV Stock Standards, 200 µg/mL

Commercial standards (typically Ultra Scientific standard ISM-320) are obtained containing decachlorobiphenyl (DCBP) and tetrachloro-*m*-xylene

(TCMX).

7.8.4 ICV Intermediate Level Standards, 1.0 µg/mL

The ICV intermediate level calibration standard for routine pesticide compounds (**8081ABICVStk**) is prepared by diluting the AB, Hexachlorobenzene, and Mirex, and surrogate stock standards (Sections 7.8.1) with hexane to a final volume of 25 mL as summarized in the table below. All compounds in the intermediate standard are at the same final concentration, i.e., 1.0 µg/mL.

Second-Source ICV Intermediate Standard

Vol of AB (mL)	Vol of Mirex Stock (mL)	Vol of Isodrin (mL)	Vol of Surrogate Stock (mL)	Vol of HCB (mL)	Final Conc (µg/mL)
0.0125	0.25	0.005	0.125	0.025	1.0

7.8.5 Routine Pesticide ICV Working Level Standard, 0.025 µg/mL (8081ICVL3)

The working level ICV standard for the routine pesticide compounds is prepared by diluting the ICV intermediate standard (Section 7.8.4) in hexane follows:

Routine Pesticide Second-Source ICV Working Level Standard

Volume of Intermediate Standard (mL)	Final Volume (mL)	Final Concentration (µg/mL)
2.5	100	0.025

7.8.6 Appendix IX ICV Working Level Standard

The working level ICV standard for the Appendix IX compounds is prepared by diluting 0.0025 mL of the second-source Appendix IX stock standard (Section 7.8.2) and 0.0025 mL of the propachlor stock with hexane to a final volume of 1 mL. The following table lists the final concentration of each pesticide:

Appendix IX ICV Working Level Standard

Pesticide	Final Concentration (µg/mL)
2,4'-DDD	0.025
2,4'-DDE	0.025
2,4'-DDT	0.025
Chlorobenzilate	0.25
Chlorpyrifos	0.125
Diallate	2.5

Pesticide	Final Concentration (µg/mL)
Propachlor	0.25
Dicofol	0.25
Kepone	0.25

Note: The LVI method ICV can be prepared from the corresponding ICV from above by mixing equal parts of the ICV above with reagent hexane (a 2x dilution).

7.9 Continuing Calibration Verification (CCV) Standards

The level 4 AB mix working calibration standard (Section 7.6.1) and the level 4 Appendix IX working calibration standard (Section 7.6.4) are used as the CCV standards.

7.10 RL Standard

The lowest concentration calibration standard (i.e., Level 1) is used as the RL standard.

7.11 Laboratory Control Standard (LCS) Spike Solution, 0.5 µg/mL

The LCS working spike stock solution is prepared by diluting 0.25 mL of the AB mix stock standard Restek 32415 (2000 ug/mL) in acetone (see Section 7.4.1) to a final volume of 10 mL in a volumetric flask. The LCS spike solution is prepared fresh each week by diluting 0.5 mL of the LCS working spike stock to a final volume of 50 mL as summarized in the table below.

The LCS for batches of aqueous samples is prepared by adding 1.0 mL of the LCS spike solution to one liter of reagent water. The LCS for batches of soil samples is prepared by adding 1.0 mL of the LCS spiking solution to 30 g of Ottawa sand.

LCS Spiking Solution

Volume of AB Mix Stock (mL)	Conc of AB Mix Stock (µg/mL)	Final Volume (mL)	Final Concentration (µg/mL)
0.5	50	50	0.5

7.12 Matrix Spike (MS) Spike Solution, 0.5 µg/mL

The working matrix spike solution is the same as the LCS spike solution (Section 7.11). Matrix spikes (MS and MSD) are prepared by adding 1.0 mL of the working spike solution to one liter of an aqueous sample or to a 30-gram soil subsample.

7.13 Toxaphene Spike Solution, 2.0 µg/mL

7.13.1 A Toxaphene stock standard solution at a concentration of 1,000 µg/mL is purchased from commercial sources. This must be from a different source than is used for the initial calibration.

7.13.2 The working Toxaphene spike solution is prepared in a 500 mL volumetric flask by adding 1.0 mL of the stock solution (Section 7.13.1) and diluting to volume with acetone.

7.13.3 Aqueous LCSs are prepared by adding 1.0 mL of the Toxaphene spike solution (Section 7.13.2) to 1.0 liter of reagent water. Soil LCSs are prepared by adding 1.0 mL of the Toxaphene spike solution (Section 7.13.2) to 30 grams of Ottawa sand.

7.13.4 Aqueous MS/MSDs are prepared by adding 1.0 mL of the Toxaphene spike solution (Section 7.13.2) to 1.0 liter of the selected aqueous sample. Soil sample MS/MSDs are prepared by adding 1.0 mL of the Toxaphene spike solution (Section 7.13.2) to 30 grams of the selected soil subsample.

7.14 Surrogate Spike Solution, 0.2 µg/mL

7.14.1 The surrogate stock solution, containing 200 µg/mL each of decachlorobiphenyl and tetrachloro-*m*-xylene (TCMX), is purchased from commercial sources.

7.14.2 The working surrogate spike solution is prepared in a 500 mL volumetric flask by adding 0.5 mL of the stock solution (Section 7.14.1) and diluting to volume with acetone.

7.14.3 For aqueous sample batches, 1.0 mL of the surrogate spike solution (Section 7.14.2) is added to each one-liter sample and QC sample. For soil sample batches, 1.0 mL of the surrogate spike solution (Section 7.14.2) is added to each 30-gram soil subsample and QC sample matrix.

7.15 Column Degradation Mix (EVAL B) (8081EvalBStk2)

7.15.1 The DDT/Endrin breakdown stock standard solution is obtained from commercial sources, with endrin at a concentration of 200 µg/mL, and 4,4'-DDT at 200 µg/mL (Accustandard M-8081-DS).

7.15.2 The working EVAL B solution is prepared in a 100 mL volumetric flask, by diluting 0.2 mL of the stock solution (Section 7.15.1) in hexane, as summarized in the following table:

Column Degradation Mix (Eval B Std) Spike Solution

Compound	Volume of Stock (mL)	Final Volume (mL)	Final Concentration (µg/mL)
Endrin	0.2	100	0.04
4,4'-DDT			0.04

7.16 Internal Standard Spiking Solution (8081_IS)

The spiking stock (BNB stock) at 2 ug/mL is prepared by diluting 0.2 mL of the commercial Internal Standard Stock from section 7.4.6 to a final volume of 100mL in hexane. Every standard, QC sample, and client sample is spiked with 15 uL of the internal standard spiking solution into 0.20 mL. This produces a concentration of 0.150 ng/mL of internal standard in each sample. For the LVI method use half of the volume of internal standard spike (7.5 uL).

7.17 Primer Mix

The concentration of the column primer mix is not critical. It generally consists of a mixture of CCV, old ICAL standards, and/or old soil LCS extracts. The primer mix is used to initialize the column and does not affect calibration or quantitation.

8.0 Sample Collection, Preservation, Shipment and Storage

8.1 Water samples are collected in pre-cleaned, amber glass bottles fitted with a Teflon-lined cap. To achieve routine reporting limits, a full one liter of sample is required. Additional one-liter portions are needed to satisfy the requirements for matrix spikes and duplicate matrix spikes.

8.2 Soil samples are collected in 8-ounce, pre-cleaned, wide-mouth jars with a Teflon-lined lid.

8.3 Samples are stored at $\leq$ 6 °C and not frozen.

8.4 Extracts are refrigerated at ≤ 6 °C.

Matrix	Sample Container	Min. Sample Size	Preservation	Extraction Holding Time	Analysis Holding Time	Reference
Waters	Amber glass	1 Liter 40 mL VOA (for LVI)	Cool, <6°C, not frozen	7 Days	40 Days from extraction	SW-846
Soils	Glass	30 grams	Cool, <6°C, not frozen	14 Days	40 Days from extraction	SW-846

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS Method Comments to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Assurance Program.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs. This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated. Any deviation or exceptions from QSM 5.0 requirements must have prior approval in the project requirements.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in the LIMS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Initial Performance Studies

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on an instrument he/she will be using. On-going proficiency must be demonstrated by each analyst on an annual basis. See Section 13.0 for more details on detection limit studies, initial demonstrations of capability, and analyst training and qualification.

9.3 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. The method blank must be run on each instrument that is used to analyze samples from the same preparation batch. See QC Policy DV-QA-003P for further details.

9.4 Method Blank (MB)

At least one method blank must be processed with each preparation batch. The method blank for batches of aqueous samples consists of 1.0 liter of reagent water (the LVI method will require a 250 mL volume of reagent water), and for batches of soil samples, consists of 30 grams of Ottawa sand, both of which are free of any of the analyte(s) of interest. The method blank is processed and analyzed just as if it were a field sample.

Acceptance Criteria: The result for the method blank must be less than one-half the reporting limit for the analyte(s) of interest. For DoD QSM 4.2 or QSM 5.0 the acceptance criteria is no analytes detected > ½ RL (i.e. LOQ) or > 1/10 the amount measured in any sample or 1/10 the regulatory limit whichever is greater.

Corrective Action: If target analytes in the blank exceed the acceptance limits, the source of the contamination must be investigated. All samples associated with an unacceptable method blank must be re-prepared and reanalyzed. If the analyte was not detected in the samples, then the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative.

See Policy DV-QA-003P and Policy DV-QA-024P for further details.

9.5 Laboratory Control Sample (LCS)

At least one LCS must be processed with each preparation batch. For aqueous sample batches, the LCS consists of reagent water to which the analyte(s) of interest are added at a known concentration. For soil sample batches, the LCS consists of reagent sand to which the analyte(s) of interest are added at a known concentration. See Section 7.11 for the preparation of LCSs. The LCS is carried through the entire analytical procedure just as if it were a sample.

Acceptance Criteria: The recovery results for the LCS must fall within the established control limits. Control limits are set at ± 3 standard deviations around the historical mean. Where required, project-specific limits may be used in place of historical limits. Current control limits are maintained in the LIMS.

When there are more than 11 analytes in the LCS, then NELAC allows a specified number of results to fall beyond the LCS control limit (3 standard deviations), but within the marginal exceedance (ME) limits, which are set at ± 4 standard deviations around the mean of historical data. The number of marginal exceedances is based on the number of analytes in the LCS, as shown in the following table:

# of Analytes in LCS	# of Allowed MEs
> 90	5
71 – 90	4
51 – 70	3
31 – 50	2
11 – 30	1
< 11	0

If more analytes exceed the LCS control limits than is allowed, or if any analyte exceeds the ME limits, the LCS fails and corrective action is necessary. Marginal exceedances must be random. If the same analyte repeatedly fails the LCS control limits, it is an indication of a systematic problem. The source of the error must be identified and corrective action taken.

Note: Some programs (e.g., South Carolina) do not allow marginal exceedances. Please see the QAS's in the public folders for the current requirements.

Corrective Action: If LCS recoveries are outside of the established control limits, and the MS/MSD recoveries are also out of control limits then the system is out of control and corrective action must occur. If recoveries are above the upper control limit and the analyte(s) of interest is not detected in samples, the data may be reported with qualifiers (check project requirements to be sure this is allowed) and it must be addressed in the project narrative. In other circumstances, the entire batch must be re-prepared and reanalyzed. If instrument maintenance and recalibration is performed and the LCS is reanalyzed as a corrective action for out of control LCS then all of the associated samples in the batch must also be reanalyzed.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

One MS/MSD pair should be processed with each preparation batch. If sufficient sample is not available for an MS/MSD then a duplicate LCS should be prepared to establish precision. For DoD QSM 4.2 or QSM 5.0, the MS/MSD must be from the project site and if insufficient sample is available to analyze the MS/MSD pair, this is documented in an NCM but no LCSD is performed. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. It is prepared in a manner similar to the LCS, but uses a real sample matrix in place of the blank matrix. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked exactly as the MS) that is prepared and analyzed along with the sample and matrix spike. Refer to Section 7.12 for preparation of matrix spikes. Some programs allow spikes to be reported for project-related samples only. Samples identified as field blanks cannot be used for the MS/MSD analysis.

Acceptance Criteria: The recovery results for the MS and MSD must fall within the established control limits, which are set at $\pm$ 3 standard deviations around the historical mean. The relative percent difference (RPD) between the MS and MSD must be less than the established RPD limit, which is set at 3 standard deviations above the historical mean. Current control limits are maintained in the LIMS.

Corrective Action: If analyte recovery or RPD falls outside the acceptance range, verify calculations, standard solutions, and acceptable instrument performance (including calibration drift). Possible errors in sample preparation must also be eliminated (e.g., spike errors, extraction issues that may impact recovery, etc.) If no problems are indicated in this investigation, the associated LCS recovery is in control, and all other QC criteria (e.g., continuing calibration verification) are met, qualified results may be reported. The situation must be described in the final report case narrative. In other circumstances, the batch must be re-prepared and reanalyzed.

9.7 Surrogate Spikes

Every calibration standard, field sample, and QC sample (i.e., method blank, LCS, LCSD, MS, and MSD) is spiked with DCB and TCMX surrogate compounds. Refer to Section 7.14 for preparation of the surrogate spike solution.

Acceptance Criteria: The recovery of each surrogate must fall within established statistical limits, which are set at ± 3 standard deviations around the historical mean.

Corrective Action: If surrogate recoveries in the method blank are outside the established limits, verify calculations, standard solutions, and acceptable instrument performance. High surrogate recoveries in the blank might be acceptable if the surrogate recoveries for the field samples and other QC samples in the batch are acceptable. Low surrogate recoveries in the blank require re-preparation and reanalysis of the associated samples, unless sample surrogate recoveries are acceptable and targeted compounds are not detected.

For field samples, surrogate recoveries are usually calculated and reported for DCB only. TCMX may also be added. If two surrogate compounds are analyzed and recoveries calculated, and either surrogate fails to meet acceptance criteria, corrective actions are required. (This also applies to programs that require the use of only one surrogate.) At least one surrogate must pass on any column from which target analytes are identified and reported.

If surrogate recoveries fail, verify calculations, standard solutions, and acceptable instrument performance. High recoveries may be due to a co-eluting matrix interference, which can be confirmed by examining the sample chromatogram, or due to the sample concentrating due to evaporation or improper adjustment of the final extract volume. Low recoveries may be due to adsorption by the sample matrix (i.e., clay particles, peat or organic material in the sample). Recalculate the data and/or reanalyze the extract if the checks reveal a problem.

If matrix interference is not obvious from the initial analysis, it is necessary to re-prepare / reanalyze a sample only once to demonstrate that poor surrogate recovery is due to a matrix effect, as long as it can be shown that the analytical system was in control. All out of control surrogates and associated corrective actions must be documented in an NCM.

9.8 Internal Standard

Acceptance Criteria: The internal standard recoveries for the opening CCVs for each 12 hour sequence must be within -50% to +100% of the response established by the midpoint of the ICAL. The internal standard response for the samples is compared to the most recent (preceding) calibration standard and must be within -50% and +100% of the response measured for that standard.

Corrective Action: If the internal standard response is outside of this range then the samples must be diluted until the recoveries are in control. Failure to meet this criteria in a CCV requires reanalysis of the standard and all affected samples analyzed in the bracket previous to the standard and after the standard. Recalibration is necessary if control cannot be established.

10.0 Calibration and Standardization

10.1 TestAmerica Denver gas chromatograph instrument systems are computer controlled to automatically inject samples and process the resulting data.

10.1.1 Detailed information regarding calibration models and calculations can be found in Corporate SOP CA-Q-P-003 *Calibration Curves and the Selection of Calibration Points* and under the public folder, *Arizona Calibration Training.*

10.1.2 Use the ChemStation chromatography data system to set up GC conditions for calibration. See Table 2 for typical operating conditions.

10.1.3 Transfer calibration standard solutions into autosampler vials and load into the GC autosampler. Use the ChemStation software to set up the analytical sequence.

10.1.4 Unprocessed calibration data are transferred to the Chrom database for processing. After processing the calibration data, print the calibration report and review it using the calibration review checklist, GC and HPLC ICAL TALS Review Checklist. (See SOP DV-QA-0020.) Submit the calibration report to a qualified peer or the group leader for final review. The completed calibration review checklist is stored in the documents section of each analytical batch in TALS.

10.2 Column Degradation Evaluation

10.2.1 Each day of operation before any calibration or calibration verification standards are analyzed and at the beginning of each 12-hour shift, the column degradation evaluation mix (EVAL B) must be analyzed. The degradation check must be performed whether or not DDT, endrin, or degradation compounds are designated as target analytes. The purpose of the evaluation is to determine whether instrument/column maintenance is needed. The preparation of this standard is described in Section 7.15.

10.2.2 The results of the analysis of the EVAL B standard solution are used to calculate column degradation in terms of DDT percent breakdown (%B) and Endrin %B as follows:

$$\text{DDT } \%B = \frac{A_{DDD} + A_{DDE}}{A_{DDD} + A_{DDE} + A_{DDT}} \times 100\% \qquad \textit{Equation 1}$$

Where A_{DDD}, A_{DDE}, and A_{DDT} are the peak responses for 4,4'-DDD, 4,4'-DDE, and 4,4'-DDT, respectively, in the EVAL B chromatogram.

$$\text{Endrin } \%B = \frac{A_{EK} + A_{EA}}{A_{EK} + A_{EA} + A_{E}} \times 100\% \qquad \textit{Equation 2}$$

Where A_{EK}, A_{EA}, and A_E are the peak responses for endrin ketone, endrin aldehyde, and endrin, respectively, in the EVAL B chromatogram.

10.2.3 Acceptance Criteria

The %B for each of these two compounds, DDT and endrin, must not be greater than 15%.

10.2.4 Corrective Action

If the breakdown of DDT and/or endrin exceeds the 15% limit, corrective action must be taken. This action may include any or all of the following:

- Replacing the injection port liner or the glass wool.
- Cutting off a portion of the injection end of the column or guard column.
- Replacing the GC column or guard column
- Replacing the y-splitter.

After taking the appropriate corrective action, the degradation evaluation standard must be reanalyzed and must pass acceptance criteria before conducting any calibration events.

10.3 The laboratory uses six calibration levels (as shown in Table 3) for the single-component pesticides. The lowest point on the calibration curve is at or below the reporting limit (RL). The highest standard defines the highest sample extract concentration that may be reported without dilution. The preparation of the calibration standards is described in Section 7.6.

10.4 All initial calibration points must be analyzed without any changes to instrument conditions, and all points must be analyzed within 24 hours.

10.5 Calibration for the multi-peak component analytes, Toxaphene and Technical Chlordane, begins with a single-point calibration at or near the RL. If any multi-peak components are found to be present in the samples, a calibration for the multi-component analyte(s) is conducted with a minimum of five calibration levels. The samples are then reanalyzed using the full calibration curve that brackets the quantitation range.

10.6 Generally, it is NOT acceptable to remove points from a calibration. If calibration acceptance criteria are not met, the normal corrective action is to examine conditions such as instrument maintenance and accuracy of calibration standards. Any problems found must be fixed and documented in the run log or maintenance log. Then the calibration standard(s) must be reanalyzed.

10.7 If no problems are found or there is documented evidence of a problem with a calibration point (e.g., obvious mis-injection explained in the run log), then one point might be rejected, but only if all of the following conditions are met:

10.7.1 The rejected point is the highest or lowest on the curve, i.e., the remaining points used for calibration must be contiguous; and

10.7.2 The lowest remaining calibration point is still at or below the project reporting limit; and

10.7.3 The highest remaining calibration point defines the upper concentration of the working range, and all samples producing results above this concentration are diluted and reanalyzed; and

10.7.4 The calibration must still have the minimum number of calibration levels required by the method, i.e., five levels for calibrations modeled with average calibration factors or linear regressions, or six levels for second-order curve fits.

10.8 If a data point is rejected, it must be documented in the sequence log and on an NCM which is filed with the project.

NOTE: Second order curves are not allowed for South Carolina work.

10.9 Internal Standard Calibration

Internal standard calibration involves the comparison of an instrument response (e.g., peak area or peak height) from the target compound in the sample to the response of the internal standard compound, which is added to the sample or sample extract prior to injection. See section 7.4 for the internal standards used. The same concentration of internal standard is added to each initial calibration standard. For each calibration level, the response factor, RF, is calculated as follows:

$$RF = \frac{A_s \times C_{is}}{A_{is} \times C_s} \qquad \textit{Equation 1}$$

Where:

A_s = Peak area (or height) of the analyte or surrogate.
A_{is} = Peak area (or height) of the internal standard.

C_s = Concentration of the analyte or surrogate, in µg/L.
C_{is} = Concentration of the internal standard, in µg/L.

10.10 Establishing the Calibration Function

Calibrations are modeled either as average calibration factors or as linear regression curves, using a systematic approach to select the optimum calibration function. Start with the simplest model, i.e., a straight line through the origin and progress through the other options until calibration acceptance criteria are met.

10.10.1 Linear Calibration Using Average Calibration Factor

The calibration factor is a measure of the slope of the calibration line, assuming that the line passes through the origin. Under ideal conditions, the factors calculated for each calibration level will not vary with the concentration of the standard. In practice, some variation can be expected. When the variation, measured as the relative standard deviation, is relatively small (e.g., ≤ 20%), the use of the straight line through the origin model is generally appropriate.

10.10.1.1 The average calibration factor is calculated as follows:

$$\overline{RF} = \frac{\sum_{i=1}^{n} RF_i}{n} \qquad \text{Equation 2}$$

Where:

RF_i = The calibration factor for the i^{th} calibration level.

n = The number of calibration levels.

10.10.1.2 The relative standard deviation (RSD) is calculated as follows:

$$RSD = \frac{SD}{\overline{RF}} \times 100\% \qquad \text{Equation 3}$$

Where SD is the standard deviation of the average RF, which is calculated as follows:

$$SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RF_i - \overline{RF}\right)^2}{n-1}} \qquad \text{Equation 4}$$

10.10.2 Evaluation of the Average Response Factor

Plot the calibration curve using the average RF as the slope of a line that passes through the origin. Examine the residuals, i.e., the difference between the actual calibration points and the plotted line. Particular attention should be paid to the residuals for the highest points, and if the residual values are relatively large, a linear regression should be considered.

Acceptance Criteria: The RSD must be ≤ 20%. SW-846 Method 8000B allows evaluation of the grand average across all compounds, but some programs (e.g., DoD, Arizona and South Carolina require evaluation of each compound individually). Check project requirements.

Corrective Action: If the RSD exceeds the limit, linearity through the origin cannot be assumed, and a least-squares linear regression should be attempted.

10.10.3 Linear Calibration Using Least-Squares Regression

Calibration using least-squares linear regression produces a straight line that does not pass through the origin. The calibration relationship is constructed by performing a linear regression of the instrument response (peak area or peak height) versus the concentration of the standards. The instrument response is treated is the dependent variable (y) and the concentration as the independent variable (x). The regression produces the slope and intercept terms for a linear equation in the following form:

$$y = ax + b \qquad \text{Equation 5}$$

Where:

- y = Instrument response (peak area or height).
- x = Concentration of the target analyte in the calibration standard.
- a = Slope of the line.
- b = The y-intercept of the line.

For an internal standard calibration, the above equation takes the following form:

Equation 6

$$\frac{A_s C_{is}}{A_{is}} = aC_s + b$$

To calculate the concentration in an unknown sample extract, the regression equations 5 and 6 are solved for concentration, resulting in the following equations, where x and C_s are now the concentration of the target analyte in the unknown sample extract:

$$x = \frac{y - b}{a} \qquad \textit{Equation 7}$$

$$C_s = \frac{\left[\frac{A_s C_{is}}{A_{is}} - b\right]}{a}$$ *Equation 8*

10.10.4 Evaluation of the Linear Least-Squares Regression Calibration Function

With an unweighted linear regression, points at the lower end of the calibration curve have less weight in determining the curve than points at the high concentration end of the curve. For this reason, inverse weighting of the linear function is recommended to optimize the accuracy at low concentrations. Note that the August 7, 1998 EPA memorandum "Clarification Regarding Use of SW-846 Methods", Attachment 2, Page 9, includes the statement "The Agency further recommends the use of this for weighted regression over the use of an unweighted regression."

Acceptance Criteria: To avoid bias in low level results, the absolute value of the y-intercept must be significantly less than the reporting limit (RL), and preferably less than the MDL.

Also examine the residuals, but with particular attention to the residuals at the bottom of the curve. If the intercept or the residuals are large, the calibration should be repeated since a higher order regression is not allowed for this method.

The linear regression must have a correlation coefficient (r) ≥ 0.99. DoD QSM 5.0 requires r^2 >0.99.

Corrective Action: If the correlation coefficient falls below the acceptance limit, the linear regression is unacceptable and the calibration should be repeated since a higher order regression is not allowed for this method.

10.10.5 Polynomial regression fits of third order or higher are not allowed for this method.

10.11 Initial Calibration Verification (ICV), 0.025 µg/mL for most compounds

A mid-level standard that is obtained from a source different from that of the calibration standards (second-source standard) is used to verify the initial calibration (see Section 7.8). The ICV standard is analyzed immediately following the initial calibration (ICAL).

Acceptance Criteria: The result for the target analyte(s) in the ICV standard must be within ± 15% for Method 8081A and ± 20% of the expected value(s) for Method 8081B.

Corrective Action: If the applicable criteria is not achieved, the ICV standard, calibration standards, and instrument operating conditions should be checked. Correct any problems and rerun the ICV standard. If the ICV still fails to meet acceptance criteria, then repeat the ICAL.

10.12 Calibration Verification

10.12.1 12-Hour Calibration Verification

NOTE: It is not necessary to run a CCV standard at the beginning of the sequence if samples are analyzed immediately after the completion of the initial calibration.

10.12.1.1 Continuing Calibration Verification (CCV), 0.05 µg/mL for most compounds.

NOTE: Arizona and Wisconsin require that the CCV concentration be varied throughout the sequence when calibration fits other than average response are used.

It may be appropriate to analyze a mid-level standard more frequently than every 12 hours. The mid-level calibration standard is analyzed as the continuing calibration verification (CCV) standard (see Section 7.9).

At a minimum, this is analyzed after every 20 samples, including matrix spikes, LCSs, and method blanks. Some programs (e.g., DOD) require analysis of a bracketing CCV every 10 field samples.

If 12 hours elapse, analyze the 12-hour standard sequence instead (including the Column Degradation Evaluation). Depending upon the program a closing CCV is not required when using an internal standard. DoD and Arizona require a bracketing CCVs.

NOTE: If a bracketing CCV is performed, the acceptance criteria in Section 10.12.3 apply to all samples.

10.12.2 RL Standard

It may also be appropriate to analyze a standard prepared at or very near the reporting limit (RL) for the method at the end of the analytical sequence, as a minimum (see Section 7.10). This standard can be used to rule out false negatives in client samples in cases where the %D for one or more of the analytes in a bracketing CCV falls below the lower acceptance limit. The results for the RL standard are not evaluated unless the previous CCV fails acceptance criteria.

10.12.3 Acceptance Criteria for Continuing Calibration Verification (CCV)

10.12.3.1 Detected Analytes (≥ RL)

For any analyte detected at or above the reporting limit (RL) in client samples, the percent difference (%D) for that analyte in the preceding and following CCVs (i.e., bracketing CCVs) or 12-hour calibration must be within ± 15% for Method 8081A and ± 20% for Method 8081B using method 8000C criteria as a reference.

DoD QSM 5.0 requires recalibration and reanalysis of all affected samples since the last acceptable CCV. As an alternative, the laboratory may analyze two additional consecutive CCVs within one hour of the failed CCV. If both pass, the samples may be reported without reanalysis. If either fails, take corrective action(s) and recalibrate: then reanalyze all affected samples since the last acceptable CCV.

If a DoD client accepts TestAmerica's Technical Specifications for DoD QSM work, samples that have no detections when a CCV has recoveries above the project acceptance limits would be reported with a case narrative comment, in addition to applying any data qualifier flags required by the project.

In some cases, the nature of the samples being analyzed may be the cause of the failing %D. When the %D for an analyte falls outside of the CCV criteria stated above, and that analyte is detected in any or all of the associated samples, then those samples must be reanalyzed (at a dilution if column damage is imminent) to prove a matrix effect. If the drift is repeated in the reanalysis, the analyst must generate an NCM for this occurrence to explain that the drift was most likely attributable to the sample matrix and that the samples may be diluted and reanalyzed to minimize the effect if so desired by the client.

Refer to Section 12 for which result to report.

In cases where additional compounds are to be analyzed in conjunction with compounds defined by this method and that are not defined in the scope and application of method 8081B different CCV acceptance criteria may apply. Kepone is not recommended by method 8081B and the CCV acceptance criteria is defined as +/- 53%. Further these additional compounds will not be used in grand mean calculations (when applicable) as discussed below.

The %D is calculated as follows:

$$\%D = \frac{\text{Measured Conc} - \text{Theoretical Conc}}{\text{Theoretical Conc}} \times 100 \qquad \textit{Equation 11}$$

10.12.3.2 Analytes Not Detected (< RL)

For any analyte not detected in client samples, the %D for that analyte in the bracketing CCVs should also be within ± 20% for Method 8081B or within 15% for Method 8081A. For method 8081B Test America Denver references method 8000C for compounds with curve fits other than an average curve fit. See also DV-QA-027P for further evaluation criteria. Any deviation for the calibration criteria outlined in this procedure must be documented in an NCM.

NOTE: The grand mean must not be applied when Method 8000C is applicable (e.g., Arizona)

10.13 Retention Time Windows

Retention time (RT) windows must be determined for all analytes.

10.13.1 Determine new RT windows each time a new column is installed or annually, whichever is most frequent.

10.13.2 Make an injection of all analytes of interest each day over a 72-hour period.

10.13.3 Calculate the mean and standard deviation for the three RTs for each analyte as follows:

$$\text{Mean RT} = \overline{RT} = \frac{\sum_{i=1}^{n} RT_i}{n} \qquad SD = \sqrt{\frac{\sum_{i=1}^{n}\left(RT_i - \overline{RT}\right)^2}{n-1}} \qquad \textit{Equations 12 \& 13}$$

Where:

RT_i = Retention time for the ith injection.
n = Number of injections (typically 3).
SD = Standard deviation.

NOTE: For the multi-component analytes, Toxaphene and Technical Chlordane, the mean and standard deviation must be calculated for each of the 3 to 6 major peaks used for sample calculations.

10.13.4 Set the width of the RT window for each analyte at ± 3 standard deviations of the mean RT for that analyte.

10.13.5 The center of the RT window for an analyte is the RT for that analyte from the last of the three standards measured for the 72-hour study.

10.13.6 The center of the window for each analyte is updated with the RT from the level 4 standard of the ICAL, or the CCV at the beginning of the analytical sequence. The width of each window remains the same until new windows are generated following the installation of a new column, or in response to an RT failure.

10.13.7 If the RT window as calculated above is less than ± 0.03 minute, use ± 0.03 minute as the RT window. This allows for slight variations in retention times caused by sample matrix.

11.0 Procedure

11.10 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP # DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative.

11.11 Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

11.12 Sample Preparation

11.12.1 Sample preparation for aqueous samples is described in SOP DV-OP-0006.

11.12.2 Sample preparation for solid samples is described in SOPs DV-OP-0016 and DV-OP-0015.

11.12.3 Cleanup and concentration of sample extracts are described in SOP DV-OP-0007. Note that it is highly recommended that all samples be check for sulfur and cleaned up if necessary before the samples are analyzed on the instrument. Sulfur can contaminate the column and hinder the quantification of certain compounds.

11.12.4 The final extract volume in hexane is 10 mL. The LVI method final volume is 5 mL.

11.12.5 Use hexane to dilute sample extracts, if necessary.

11.13 Instrument Maintenance and Troubleshooting

Before the start of any daily sequence the instrument system should be evaluated for possible maintenance. Typically for the 8081 analysis the injection port liner must be changed daily in order to facilitate a passing DDT/Endrin breakdown standard. If the previous run ended with a failing continuing calibration then the system should be maintained to bring it back into control. The injector septum should be changed after about 200 injections have been completed. If the last CCV that was analyzed indicated a high response then a simple liner change is typically sufficient to bring the system back into control. Analysis of a few solvent blanks or a system bake out may be necessary to drive out any residual contamination on the column. A reduced response may indicate that the system needs to be evaluated for leaks. Poor peak shape may necessitate clipping a loop out of the analytical column. If this fails to solve the peak shape problem then replacement of the columns may be indicated. The goal is to maintain the system as close to top condition as possible as was observed when new columns and injector parts were installed. Re-calibration should not be used to correct for maintenance related issues. Always document any maintenance procedure in the maintenance logbook.

11.14 Gas Chromatography

Chromatographic conditions for this method are presented in Table 2. Use the ChemStation interface to establish instrument operating conditions for the GC. Raw data obtained by the ChemStation software is transferred to the Chrom database for further processing. The data analysis method, including peak processing and integration parameters, calibration, RT windows, and compound identification parameters, is set up in the Chrom software.

11.15 Sample Introduction

All extracts and standards are allowed to warm to room temperature before injection. An autosampler is used to introduce samples into the chromatographic system by direct injection of 1 or 2 µL of the sample extract. Samples, standards, and QC samples must be introduced using the same procedure. Use the ChemStation interface to set up and run the analytical sequence. Sample injection and analysis are automated and may proceed unattended.

11.16 Analytical Sequence

An analytical sequence starts with a minimum five-level initial calibration (ICAL) or a daily calibration verification. Refer to Table 3 for the calibration levels used.

11.16.1 Prior to analyzing any calibration or calibration verification standards, the column degradation evaluation standard is injected and the results are evaluated as described in Section 10.2.

11.16.2 The daily calibration verification includes analysis of the 12-hour calibration sequence (Section 10.12.1) and updating the retention time windows (see Section 10.13).

11.16.3 If there is a break in the analytical sequence of greater than 12 hours, a new analytical sequence must be started with a daily calibration verification.

11.16.4 The following is a typical analytical sequence:

- Primer

- Hexane blank
- Eval B Std (column degradation evaluation)
- Daily initial CCVs
- LCS
- Method Blank
- 10 samples
- CCVs
- Followed by cycles of 10 samples and CCVs as needed
- Closing CCV

11.17 Daily Retention Time Windows

The centers of the retention time (RT) windows determined in Section 10.13 are adjusted to the RT of each analyte as determined in the 12-hour calibration verification. The centers of the RT windows must be updated at the beginning of each analytical sequence.

11.18 Manual Integration and Data Review

Upon completion of the analytical sequence, transfer the raw chromatography data to the CHROM database for further processing.

11.18.1 Review chromatograms online and determine whether manual data manipulations are necessary.

11.18.2 All manual integrations must be justified and documented. See DV-QA-011P requirements for manual integration.

11.18.3 Manual integrations may be processed using an automated macro, which prints the before and after chromatograms and the reason for the change, and attaches the analyst's electronic signature.

11.18.4 Alternatively, the manual integration may be processed manually. In the latter case, print both the before and after chromatograms and record the reason for the change and initial and date the after chromatogram. Before and after chromatograms must be of sufficient scale to allow an independent reviewer to evaluate the manual integration. The manually processed chromatograms must be scanned and attached to the project in TALS.

11.19 Compile the raw data for all the samples and QC samples in a batch. The analytical batch is defined as containing no more than 20 samples, which include field samples and the MS and MSD.

11.19.1 The data package should consist of the checklist, sequence(s), ICAL cover, ICAL summary and history used for data quantitation and the prep batch paperwork.

11.19.2 Perform a level 1 data review and document the review on the data review checklist, GC Data Review Checklist/Batch Summary (See SOP DV-QA-0020.)

11.19.3 Submit the data package and review checklist to the Data Review Group for the level 2 review. All manual integrations must be evaluated by the peer reviewer and this review must be documented by date and initial on the level 2 review checklist. The level 2 review is documented on the review checklist initiated at the level 1 review. The data review process is explained in SOP DV-QA-0020.

12.0 Calculations / Data Reduction

12.10 Qualitative Identification

12.10.1 Tentative identification of an analyte occurs when a peak is found on the primary column within the RT window for that analyte, at a concentration above the reporting limit, or above the MDL if qualified data (J flags) are to be reported. Identification is confirmed if a peak is also present in the RT window for that analyte on the second (confirmatory) column and if the analyte concentration is greater than the MDL. When confirmation is made using a second column, the analysis on the second column must meet all of the QC criteria for continuing calibration verification and RTs.

12.10.2 The experience of the analyst should weigh heavily in the interpretation of the chromatogram. For example, sample matrix or laboratory temperature fluctuation may result in variation of retention times. If a RT shift greater than the RT window occurs for a reported compound the situation must be explained in an NCM.

12.11 Dual-Column Quantitation and Reporting

12.11.1 A primary column is designated. The result from the primary column is normally reported. If the continuing calibration verification fails on one of the columns, the appropriate corrective action must be taken. The result from the secondary (confirmation) column may be reported if either of the following possibilities are true:

12.11.1.1 There is obvious chromatographic interference on the primary column.

12.11.1.2 The result on the primary column is > 40% greater than the result on the secondary column.

12.11.2 For DoD QSM 4.2 or QSM 5.0 work, calibration and QC criteria for the second column are the same as for the initial or primary column analysis.

12.11.3 **Dual Column Results With >40% RPD**

12.11.3.1 If the relative percent difference (RPD) between the responses on the two columns is greater than 40%, the higher of the two results is reported unless there is obvious interference documented on the chromatogram.

12.11.3.2 If there is visible positive interference, e.g., co-eluting peaks, elevated baseline, etc., for one column and not the other, then report the results from the column without the interference with the appropriate data qualifier flag, footnote, and/or narrative comment in the final report.

12.11.3.3 If there is visible positive interference for both columns, then report the lower of the two results with the appropriate flag, footnote, and/or narrative comment in the final report.

12.11.3.4 The RPD between two results is calculated using the following equation:

$$RPD = \frac{|R_1 - R_2|}{\frac{1}{2}(R_1 + R_2)} \times 100\% \qquad \textit{Equation 14}$$

Where R_1 is the result for the primary column and R_2 is the result for the confirmation column.

12.12 Multi-Component Analytes (Toxaphene and Technical Chlordane)

12.12.1 Qualitative Identification

Retention time windows are also used for identification of multi-component analytes, but the “fingerprint” produced by major peaks of those compounds in the standard is used in tandem with the retention times to identify the compounds. The ratios of the areas of the major peaks are also taken into consideration. Identification of these compounds may be made even if the retention times of the peaks in the sample fall outside of the retention time windows of the standard, if in the analyst’s judgment the fingerprint (retention time and peak ratios) resembles the standard chromatogram.

12.12.2 Quantitation of Toxaphene

12.12.2.1 While Toxaphene contains a large number of compounds that produce well resolved peaks in a GC/ECD chromatogram, it also contains many other components that are not chromatographically resolved. The unresolved complex mixture results in a "hump" in the chromatogram that is characteristic of the Toxaphene mixture of compounds. The resolved peaks are important for the identification of the mixture, and the area of the unresolved complex mixture contributes a significant portion of the area of the total response.

12.12.2.2 To measure total area, construct the baseline of Toxaphene in the sample chromatogram between the RTs of the first and last eluting Toxaphene components in the standard. In order to use the total area approach, the pattern in the sample chromatogram must be compared to that of the standard to ensure that all of the major components in the standard are present in the sample. Otherwise, the sample concentration may be significantly underestimated.

12.12.2.3 Toxaphene may also be quantitated on the basis of 4 to 6 major peaks. Using a subset of 4 to 6 peaks for quantitation provides results that agree well with the total peak approach and may avoid difficulties when interferences with Toxaphene peaks are present in the early portion of the chromatogram from compounds such as DDT. Construct the baseline as outlined in 12.3.2.2.

12.12.2.4 When Toxaphene is determined using the 4 to 6 peaks approach, care must be taken to evaluate the relative areas of the peaks chosen in the sample and standard chromatograms.

12.12.2.5 The chosen peaks must be within the established retention time. If there is an interference that affects the accuracy of results, the analyst may use as few as 4 major peaks. The same peaks that are used for sample quantitation must be used for calibration.

12.12.2.6 The heights or areas of the chosen peaks should be summed together and averaged to determine the Toxaphene concentration.

12.12.2.7 Second column confirmation of multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

NOTE: DoD projects require the use of second-column confirmation of multi-component analytes unless the project work plans (SOW, SAP, QAPP, etc.) specify single-column analysis. Method comments must indicate any projects or programs that require second-column confirmation for multi-component analytes.

12.12.3 Quantitation of Technical Chlordane

12.12.3.1 Technical Chlordane is a mixture of at least 11 major components and 30 or more minor components that is used to prepare specific pesticide formulations. *cis*-Chlordane (or α-Chlordane) and *trans*-Chlordane (or γ-Chlordane) are the two most prevalent major components of Technical

Chlordane. However, the exact percentage of each in the technical material is not completely defined, and is not consistent from batch to batch.

12.12.3.2 When the GC pattern of the sample resembles that of Technical Chlordane, Chlordane may be quantitated by comparing the total area of the Chlordane chromatogram using 3 to 5 major peaks or the total area. If the Heptachlor epoxide peak is relatively small, include it as part of the total Chlordane area for calculation. If Heptachlor and/or Heptachlor epoxide are much out of proportion, calculate these separately and subtract their areas from the total area to give a corrected Chlordane area.

NOTE: Octachlor epoxide, a metabolite of Chlordane, can easily be mistaken for Heptachlor epoxide on a nonpolar GC column.

12.12.3.3 To measure the total area of the Chlordane chromatogram, construct the baseline of Technical Chlordane in each calibration chromatogram between the RTs of the first and last eluting Technical Chlordane components. Use this area and the mass or concentration of Technical Chlordane in each calibration standard to establish the calibration function (Section 10.0). Construct a similar baseline in the sample chromatogram, measure the area, and use the calibration function to calculate the concentration in the sample extract.

12.12.3.4 When the GC pattern of Chlordane in a sample differs considerably from that of the Technical Chlordane standard, it may be practical to report "Chlordane (not otherwise specified, CAS number 57-74-9)." Using the same process and calibration as for reporting Technical Chlordane.

12.12.3.5 A third option for quantitating Technical Chlordane is to quantitate the peaks for α-Chlordane, γ-Chlordane, and Heptachlor separately against the appropriate reference materials, and report these individual components under their respective CAS numbers.

NOTE: See Section 12.15.2 for use of CLD Flag when only the isomers are reported and Technical Chlordane is the requested analyte.

12.12.3.6 Second column confirmation of multi-component analytes will only be performed when requested by the client, because the appearance of the multiple peaks in the sample usually serves as a confirmation of analyte presence.

NOTE: DoD projects require the use of second-column confirmation of multi-component analytes unless the project work plans (SOW, SAP, QAPP, etc.) specify single-column analysis.

12.13 Surrogate recovery results are calculated and reported for DCB. TCMX may also be added, however if the two surrogate compounds are analyzed, and recoveries are calculated, and either surrogate fails to meet control limits, corrective actions are required (this also applies to programs that require the use of only one surrogate). See section 9.7 for further details.

12.14 Calibration Range and Sample Dilutions

12.14.1 If the concentration of any analyte exceeds the working range as defined by the calibration standards, then the sample must be diluted with hexane (record the hexane lot number in the run sequence) and reanalyzed. Dilutions should target the most concentrated analyte in the upper half (over 50% of the high level standard) of the calibration range. Samples that were analyzed immediately following the high sample must be evaluated for carryover. If the samples have results at or above the RL for the analyte(s) that were found to be over the calibration range in the high sample, they must be reanalyzed to rule out carryover, unless other objective evidence indicates that the detection is not the result of carryover. Such evidence may include an observation where carryover was not observed when samples or blanks were analyzed after another sample with similar high compound recovery or when the detection in the sample with suspected carryover is much higher than the expected amount of carryover (i.e. the sample's concentration may be similar to or higher than the concentration found in the previous sample). It may also be necessary to dilute samples because of matrix interferences.

12.14.2 If the initial diluted run has no hits or hits below 20% of the calibration range, and the matrix allows for analysis at a lesser dilution, then the sample must be reanalyzed at a dilution targeted to bring the largest hit above 50% of the calibration range.

12.14.3 Guidance for Dilutions Due to Matrix Interference

If the sample is initially run at a dilution and only minor matrix peaks are present, then the sample should be reanalyzed at a more concentrated dilution. Analyst judgment is required to determine the most concentrated dilution that will not result in instrument contamination. Ideally, the dilution chosen will make the response of the matrix interferences equal to approximately half the response of the mid-level calibration standard.

12.14.4 Reporting Dilutions

Some programs (e.g., South Carolina and AFCEE) and some projects require reporting of multiple dilutions (check special requirements in LIMS). In other cases, the most concentrated dilution with no target compounds above the calibration range will be reported. When reporting multiple dilutions, unless otherwise requested, the analyst typically reports the lowest dilution practical (one that is not obscured by the matrix) and then one or two higher dilutions so that the bulk of the detections are quantifiable and all of the compounds are within the calibration range.

12.15 Interferences Observed in Samples

12.15.1 Dual column analysis does not entirely eliminate interfering compounds. Complex samples with high background levels of interfering organic compounds can produce false positive and/or false negative results. The analyst must use appropriate judgment to take action as the situation warrants.

12.15.2 Suspected Negative Interferences

If peak detection is prevented by interferences, further cleanup should be attempted (see SOP DV-OP-0007). Elevation of reporting levels and/or lack of positive identification must be addressed in the case narrative.

If the individual isomers of chlordane are identified, but there is no pattern for the confirmation of "Technical Chlordane", and the project has ONLY technical chlordane requested, the results for technical chlordane should be qualified ("CLD") by the analyst to indicate the presence of the chlordane isomers.

12.15.3 Suspected Positive Interferences

If no further cleanup is reasonable and interferences are evident that are suspected of causing false positive results, consult with the laboratory Project Manager to determine if analysis using additional confirmation techniques is appropriate for the project. Use of additional confirmation columns is another possible option, however caution is warranted in order to rule out false negatives. At a minimum, an NCM should be prepared by the analyst and should include the following comment for inclusion in the case narrative:

"*Based on review of the chromatograms for samples _____, it is my opinion that the evident interferences may be causing false results.*

Date ____________ Analyst ____________________"

Sample dilution may be the only acceptable recourse to resolve detections when large amounts of non-target matrix are observed.

12.16 Calculations

12.16.1 LCS and Surrogate Spike Recovery Calculation

LCS and surrogate spike recoveries are calculated using the following equation:

$$\%\text{Recovery} = \frac{\text{Concentration (or amount) found}}{\text{Concentration (or amount) spiked}} \times 100\% \qquad \textit{Equation 15}$$

12.16.2 MS and MSD Recovery Calculation

Matrix spike recoveries are calculated as follows:

$$\text{MS or MSD \%Recovery} = \left(\frac{SSR - SR}{SA}\right) \times 100\% \qquad \textit{Equation 16}$$

Where:

SSR = Measured concentration in spiked sample.
SR = Measured concentration in unspiked sample.
SA = Concentration of spike added to sample.

12.16.3 MS/MSD RPD Calculation

The relative percent difference between the MS and MSD is calculated as follows:

$$\%RPD = \frac{|R_1 - R_2|}{\frac{1}{2}(R_1 + R_2)} \times 100\% \qquad \textit{Equation 17}$$

Where R_1 is the result for the MS and R_2 is the result for the MSD.

12.16.4 Concentration of Analyte in the Sample Extract

Depending on the calibration function used, the concentration of the analyte in the sample extract is calculated as follows (see Section 10.0 for details on establishing the calibration function):

Average Calibration Factor: $C_e = \dfrac{A_s}{\overline{\overline{CF}}}$ *Equation 18*

Linear Regression: $C_e = \dfrac{[A_s - b]}{a}$ *Equation 19*

Non-Linear Regression: $C_e = f(A_s)$ *Equation 20*

Where:

C_e = Concentration of the analyte in the sample extract (ng/mL).
A_s = Peak area for the analyte in the sample extract injection.
b = y-intercept of the calibration fit.
a = Slope of the calibration fit.
$f(A_s)$ = Mathematical function established by the non-linear regression.

12.16.5 Concentration of Analyte in Original Sample (for 1 uL injection)

$$C_{sample} = \frac{C_e}{1000\frac{ng}{\mu g}} \times \frac{V_e}{V_s} \times DF \qquad \textit{Equation 21}$$

Where:

C_{sample}	=	Concentration of analyte in original sample (µg/L or µg/kg).
C_e	=	Concentration of analyte in sample extract injected in GC (ng/mL).
$1000\frac{ng}{\mu g}$	=	Factor to convert ng/mL to µg/mL.
V_e	=	Volume of sample extract (mL).
V_s	=	Volume (or weight) of original sample (L or kg).
DF	=	Dilution Factor (post extraction dilutions)

12.17 All data are subject to two levels of review, which is documented on a checklist, as described in SOP DV-QA-0020.

13.0 Method Performance

13.10 Method Detection Limit (MDL)

The method detection limit (MDL) is the lowest concentration that can be detected for a given analytical method and sample matrix with 99% confidence that the analyte is present. The MDL is determined according to the laboratory's MDL policy in DV-QA-005P. MDLs reflect a calculated (statistical) value determined under ideal laboratory conditions in a clean matrix, and may not be achievable in all environmental matrices. The laboratory maintains MDL studies for analyses performed; these are verified at least annually unless method or program requirements require a greater frequency.

13.11 Demonstration of Capabilities

All personnel are required to perform an initial demonstration of proficiency (IDOC) on the instrument they will be using for analysis prior to testing samples. On-going proficiency must be demonstrated annually. IDOCs and on-going proficiency demonstrations are conducted as follows.

13.11.1 Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid- level calibration.

13.11.2 Calculate the average recovery and standard deviation of the recovery for each analyte of interest.

13.11.3 If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.11.4 Further details concerning demonstrations of proficiency are described in SOP DV-QA-0024.

13.12 Training Requirements

13.12.1 The Group Leader is responsible for ensuring that this procedure is performed by an associate who has been properly trained in its use and has the required experience. See requirements for demonstration of analyst proficiency in SOP DV-QA-0024.

14.0 Pollution Control

Standards and reagents are prepared in volumes consistent with laboratory use to minimize the volume of expired standards and reagents requiring disposal.

15.0 Waste Management

15.10 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

15.11 The following waste streams are produced when this method is carried out:

15.11.1 Expired Chemicals/Reagents/Standards – Contact Waste Coordinator

15.11.2 Expired extract vial waste - Waste Stream A

NOTE: Radioactive and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of radioactive or potentially radioactive waste generated by this procedure.

16.0 References

16.10 SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005.

16.11 Method 3510C, Separatory Funnel Liquid-Liquid Extraction, Revision 3, December 1996.

16.12 Method 3550B, Ultrasonic Extraction, Revision 2, December 1996.

16.13 Method 3550C, Ultrasonic Extraction, Revision 3, February 2007.

16.14 Method 3546, Microwave Extraction, Revision 0, February 2006.

16.15 Method 3620C, Florisil Cleanup, Revision 3, February 2007.

16.16 Method 3660B, Sulfur Cleanup, Revision 2, December 1996.

16.17 Method 3665A, Sulfuric Acid/Permanganate Cleanup, Revision 1, December 1996.

16.18 Method 8081A, Organochlorine Pesticides by Gas Chromatography, Revision 1, December 1996

16.19 Method 8081B, Organochlorine Pesticides by Gas Chromatography, Revision 2, February, 2007.

16.20 Method 8000B, Determinative Chromatographic Separations, Revision 2, December, 1996.

16.21 Method 8000C, Determinative Chromatographic Separations, Revision 3, March 2003.

17.0 Method Modifications:

Item	Method	Modification
1	8081A 8081B	Method 8081B includes an internal standardization option. Because of the high probability of interferences affecting internal standards, this SOP allows only external standards.
2	8081A 8081B	Section 11.4.1.1, allows the use of a single-point calibration for the multi-component pesticides. In this SOP an initial single-point calibration is used, but a five-point calibration followed by reanalysis of associated samples is required when one of the multi-component pesticides is detected.
3	8081A 8081B	Method 8081 references 8000, which allows the use of third-order calibration curves. TestAmerica Denver does not allow third-order curves.
4	8081A 8081B 8000B	Section 10.7.2 excludes the use of the grand average of % RSD and requires each compound meet % RSD criteria for the initial calibration while Method 8000 B allows acceptance using the mean of % RSD for all compounds in the calibration.
5	8081A 8081B 8000B 8000C	Minimum retention time window ($\pm$ 0.01 minute) is more stringent than the Method 8000B window of $\pm$ 0.03 minute. The established window may be adjusted based on RT drift observed in the ICAL.
6	8081B	Section 11.5.2.1 – Use 8000C criteria for calibration verification when a non-average curve fit is used.

18.0 Tables and Attachments

Table 1: Analyte List and Standard Reporting Limits
Table 2: Typical Instrument Conditions
Table 3: Calibration Levels (μg/mL)
Table 4: LVI Method Calibration Levels (μg/mL)
Table 5: Column Degradation Evaluation Mix

Table 6: LCS/Matrix Spike and Surrogate Spike Levels
Table 7: Evaluation Criteria and Corrective Actions for Continuing Calibration Verification
Attachment 1: Example Chromatogram – AB Standard
Attachment 2: Example Chromatogram – AP9 Standard
Attachment 3: Example Chromatogram – Chlordane (Technical)
Attachment 4: Example Chromatogram – Toxaphene

19.0 Revision History

- Revision 10, dated 31 July 2015
  - Added use of Internal Standard (1-bromo-2-nitrobenzene) throughout. Calibration changed from external standard to internal standard (Sections 7, 10.9, 10.10). Changed "calibration factor" to "response factor" throughout.
  - Removed conflicting text for MB acceptance in DOD program in corrective action section of Section 9.4.
  - Updated SOP reference in Section 10.1.1 to revised corporate document number.
  - Revised section 10.12 to eliminate redundant language
  - Revised Section 10.13.7 to correct minimum RT window to $\pm$ 0.03 from $\pm$ 0.01. The latter is the minimum standard deviation to be used.
- Revision 9, dated 31 October 2014
  - Added instrument model numbers in Section 6.1
  - Identified where columns are used, by instrument in Section 6.4
  - Added more information regarding GC supplies in Section 6.6
  - Updated network location references to address current practice
  - Added TALS standard IDs throughout section 7
  - Added propachlor to the analyte list for water and throughout the SOP as needed.
  - Added criteria for DoD QSM 5.0 throughout
- Revision 8, dated 31 October 2013
  - Formatting updates
  - Section 1.3 – Removed reference to microwave LVI extractions
  - Section 2.1.1. 9.4 – Listed appropriate information for LVI procedure
  - Section 2.1.3, 4.1, 7.15.1, 7.15.2 (table), 10.1.14, 10.12.4.1, 10.12.4.2, 11.3.4, 11.5, 12.3.3.4, 12.5.4, Table 2, Table 3 (AP9 Standards), Table 4 (Chlordane Technical & Toxaphene, AP9 Standards, Surrogates), Table 5 – Added details to reflect current practices
  - Section 7.4 – Revised standard mix information
  - Section 7.5.1 – Updated table
  - Section 7.6.2 – Added detail and calibration levels
  - Section 7.6.4 – Added level 1 calibration standard and updated subsequent levels
  - Section 7.7 & 7.8 – Revised Standard detail and update section tables
  - Section 13 – Update MDL and IDOC/DOC information
  - Section 17 – Added item number 6 in the method modification table
  - Added table 8 – Chrom Peak and Peak Numbers
  - Updated attachments with Chrom chromatograms for AB mix, AP9 mix, Chlordane (Technical) and Toxaphene as attachments 1 – 4.
- Revision 7.0, dated 12 October 2012
  - Added section 1.5 to state that the LVI procedure is not approved by South Carolina

- Revision 6.0, dated 16 July 2012
  - Corrected grammatical and formatting errors.
  - Added the information on the LVI procedure throughout the SOP
  - Added paragraph on “reagent grade” materials to Section 7
  - Added Section 11.4 – Instrument Maintenance
  - Updated Table 1 to include LVI information
  - Added Table 3
- Revision 5.0, dated 30 June 2011
  - Combines SOP No. DV-GC-0020 and SOP No. DV-GC-0026, superseding the latter, implemented 28 February 2011.
  - Updated equipment and supplies section
  - Aligned language with other GC SOPs for clarity and consistency in calibration and data review sections
  - Updated standards and reporting limits table.
  - Revised reporting criteria in Section 12.2

Earlier revision histories have been archived and are available upon request.

Table 1. Analyte List and Standard Reporting Limits

Compound	Water Reporting Limit (µg/L) [1 L sample]	Water Reporting Limit (µg/L) [LVI]	Soil Reporting Limit (µg/kg)
Aldrin	0.05	0.05	1.7
α-BHC	0.05	0.05	1.7
β-BHC	0.05	0.05	1.7
δ-BHC	0.05	0.05	1.7
γ-BHC (Lindane)	0.05	0.05	1.7
α-Chlordane	0.05	0.05	1.7
γ-Chlordane	0.05	0.05	1.7
Chlordane (technical)	0.5	0.5	25
Chlorobenzilate*	0.10	0.10	30
Chlorpyrifos*	0.05	0.1	–
DBPP***	2.50	2.50	140
2,4'-DDD*	0.05	0.05	0.33
4,4'-DDD	0.05	0.05	1.7
2,4'-DDE*	0.05	0.05	0.33
4,4'-DDE	0.05	0.05	1.7
2,4'-DDT*	0.05	0.05	0.33
4,4'-DDT	0.05	0.05	1.7
Diallate*	1.0	5.0	33
Dicofol*	1.0	10.0	–
Dieldrin	0.05	0.05	1.7
Endosulfan I	0.05	0.05	1.7
Endosulfan II	0.05	0.05	1.7
Endosulfan Sulfate	0.05	0.05	1.7
Endrin	0.05	0.05	1.7
Endrin Aldehyde	0.05	0.05	1.7
Endrin Ketone	0.05	0.05	1.7
Heptachlor	0.05	0.05	1.7
Heptachlor Epoxide	0.05	0.05	6.7
Hexachlorobenzene	0.05	0.05	1.7
Isodrin	0.10	0.10	1.7
Kepone**	1.0	1.0	75
Methoxychlor	0.10	0.10	3.3
Mirex	0.05	0.05	1.7
Propachlor	0.5	0.5	-
Toxaphene	2.0	2.0	67

* These are non-routine compounds that require a separate calibration, and are analyzed only upon request.

** The laboratory has some clients with permits requiring kepone by method 8081A and 8081B. However, the method warns that kepone may change form during extraction and shift out of the expected retention time window. Kepone is <u>not</u> recommended by 8081A and 8081B.

*** Available for analysis by method 8081A only.

Table 2. Typical Instrument Conditions

Parameter	Recommended Conditions*
Injection port temperature	200 ^{o}C
Detector temperature	325 ^{o}C
Column 1 (HP6890 GC)	Rtx® CLPI: 30 m X 0.32 mm id, 0.5 µm
Column 2 (HP6890 GC)	Rtx®CLPII: 30 m X 0.32 mm id, 0.25 µm
HP6890 GC Temperature program and inlet pressure Columns 1 and 2	110 ^{o}C for 1 minute 35 ^{o}C/min to 180 ^{o}C 20 ^{o}C/min to 200 ^{o}C 35 ^{o}C/min to 235 ^{o}C and hold for 1 minute 25 ^{o}C/min to 300 ^{o}C and hold for 4 minutes 40 ^{o}C/min to 310 ^{o}C Pressure 20 psi, pulse to 40 psi for 1 minute
Column 3 (HP6890 GC)	DB-35MS: 30 m X 0.32 mm id, 0.5 µm
Column 4 (HP6890 GC)	DB-XLB: 30 m X 0.32 mm id, 0.5 µm
HP6890 GC Temperature program Columns 3 and 4	110 ^{o}C for 1 minute 35 ^{o}C/min to 245 ^{o}C and hold for 1.5 minutes 25 ^{o}C/min to 300 ^{o}C and hold for 4 minutes 40 ^{o}C/min to 310 ^{o}C
Injection	1 or 2 µL (for LVI)
Carrier gas	Hydrogen
Make up gas	Nitrogen, 60 mL/min
Y splitter	Restek or J&W or Supelco glass tee (Siltek)

* Variations in instrument conditions may exist in order to facilitate compound separation or to accommodate matrix effects from sample analysis.

NOTE: 4,4'-DDE and dieldrin are closely eluting pairs on the HP-5 column . Endosulfan II and 4,4'-DDD are closely eluting pairs on the 1701 column. For these reasons, these columns are no longer in use in the laboratory.

Table 3. Calibration Levels (µg/mL)

	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6
Individual Mix AB						
Aldrin	0.004	0.01	0.025	0.05	0.075	0.10
α-BHC	0.004	0.01	0.025	0.05	0.075	0.10
β-BHC	0.004	0.01	0.025	0.05	0.075	0.10
δ-BHC	0.004	0.01	0.025	0.05	0.075	0.10
γ-BHC (Lindane)	0.004	0.01	0.025	0.05	0.075	0.10
α-Chlordane	0.004	0.01	0.025	0.05	0.075	0.10
γ-Chlordane	0.004	0.01	0.025	0.05	0.075	0.10
4,4'-DDD	0.004	0.01	0.025	0.05	0.075	0.10
4,4'-DDE	0.004	0.01	0.025	0.05	0.075	0.10
4,4'-DDT	0.004	0.01	0.025	0.05	0.075	0.10
Dieldrin	0.004	0.01	0.025	0.05	0.075	0.10
Endosulfan I	0.004	0.01	0.025	0.05	0.075	0.10
Endosulfan II	0.004	0.01	0.025	0.05	0.075	0.10
Isodrin	0.004	0.01	0.025	0.05	0.075	0.10
Endrin	0.004	0.01	0.025	0.05	0.075	0.10
Endrin Aldehyde	0.004	0.01	0.025	0.05	0.075	0.10
Endrin Ketone	0.004	0.01	0.025	0.05	0.075	0.10
Heptachlor	0.004	0.01	0.025	0.05	0.075	0.10
Heptachlor Epoxide	0.004	0.01	0.025	0.05	0.075	0.10
Hexachlorobenzene	0.004	0.01	0.025	0.05	0.075	0.10
Methoxychlor	0.004	0.01	0.025	0.05	0.075	0.10
Endosulfan Sulfate	0.004	0.01	0.025	0.05	0.075	0.10
Mirex	0.004	0.01	0.025	0.05	0.075	0.10
Multicomponent Standards						
Chlordane (Technical)	0.10	0.20	0.50	1.0	2.0	N/A
Toxaphene	0.20	0.50	1.0	2.0	5.0	10.0
Surrogates are included the AB Mix calibration mix at the following levels:						
Tetrachloro-*m*-xylene	0.005	0.10	0.025	0.05	0.075	0.10
Decachlorobiphenyl	0.005	0.10	0.025	0.05	0.075	0.10

Appendix IX Standards:							
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
2,4'-DDD	0.001	0.005	0.010	0.025	0.035	0.05	0.10
2,4'-DDE	0.001	0.005	0.010	0.025	0.035	0.05	0.10
2,4'-DDT	0.001	0.005	0.010	0.025	0.035	0.05	0.10
Chlorobenzilate	0.01	0.050	0.10	0.25	0.35	0.5	1.0
Chlorpyrifos	0.005	0.025	0.050	0.125	0.175	0.25	0.5
DBPP	0.50	0.250	0.5	1.25	1.75	2.5	5.0
Diallate	0.250	0.50	1.0	2.5	3.5	5	10.
Dicofol	0.01	0.050	0.10	0.25	0.35	0.5	1.0
Propachlor	0.01	0.050	0.10	0.25	0.35	0.5	1.0
Kepone	0.01	0.050	0.10	0.25	0.35	0.5	1.0

Table 4. LVI method. Calibration Levels (µg/mL)

	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	
Individual Mix AB							
Aldrin	0.002	0.005	0.0125	0.025	0.0375	0.05	
α-BHC	0.002	0.005	0.0125	0.025	0.0375	0.05	
β-BHC	0.002	0.005	0.0125	0.025	0.0375	0.05	
δ-BHC	0.002	0.005	0.0125	0.025	0.0375	0.05	
γ-BHC (Lindane)	0.002	0.005	0.0125	0.025	0.0375	0.05	
α-Chlordane	0.002	0.005	0.0125	0.025	0.0375	0.05	
γ-Chlordane	0.002	0.005	0.0125	0.025	0.0375	0.05	
4,4'-DDD	0.002	0.005	0.0125	0.025	0.0375	0.05	
4,4'-DDE	0.002	0.005	0.0125	0.025	0.0375	0.05	
4,4'-DDT	0.002	0.005	0.0125	0.025	0.0375	0.05	
Dieldrin	0.002	0.005	0.0125	0.025	0.0375	0.05	
Endosulfan I	0.002	0.005	0.0125	0.025	0.0375	0.05	
Endosulfan II	0.002	0.005	0.0125	0.025	0.0375	0.05	
Isodrin	0.002	0.005	0.0125	0.025	0.0375	0.05	
Endrin	0.002	0.005	0.0125	0.025	0.0375	0.05	
Endrin Aldehyde	0.002	0.005	0.0125	0.025	0.0375	0.05	
Endrin Ketone	0.002	0.005	0.0125	0.025	0.0375	0.05	
Heptachlor	0.002	0.005	0.0125	0.025	0.0375	0.05	
Heptachlor Epoxide	0.002	0.005	0.0125	0.025	0.0375	0.05	
Hexachlorobenzene	0.002	0.005	0.0125	0.025	0.0375	0.05	
Methoxychlor	0.002	0.005	0.0125	0.025	0.0375	0.05	
Endosulfan Sulfate	0.002	0.005	0.0125	0.025	0.0375	0.05	
Mirex	0.002	0.005	0.0125	0.025	0.0375	0.05	
Multicomponent Standards							
Chlordane (Technical)	0.025	0.1	0.25	0.50	1.0	2.0	
Toxaphene	0.1	0.25	0.5	1.0	2.5	5.0	
Appendix IX Standards:							
	Level 1	Level 2	Level 3	Level 4	Level 5	Level 6	Level 7
2,4'-DDD	0.0005	0.0025	0.005	0.0125	0.0175	0.025	0.05
2,4'-DDE	0.0005	0.0025	0.005	0.0125	0.0175	0.025	0.05
2,4'-DDT	0.0005	0.0025	0.005	0.0125	0.0175	0.025	0.05
Chlorobenzilate	0.005	0.025	0.05	0.125	0.175	0.25	0.5
Chlorpyrifos	0.0025	0.0125	0.025	0.0625	0.0875	0.125	0.25
DBPP	0.25	0.125	0.25	0.625	0.875	1.25	2.5
Diallate	0.125	0.25	0.5	1.25	1.75	2.5	5.0
Dicofol	0.005	0.025	0.05	0.125	0.175	0.25	0.5
Propachlor	0.005	0.025	0.05	0.125	0.175	0.25	0.5
Kepone	0.005	0.025	0.05	0.125	0.175	0.25	0.5
Surrogates are included the AB Mix calibration mix at the following levels:							
Tetrachloro-*m*-xylene	0.002	0.005	0.0125	0.025	0.0375	0.05	
Decachlorobiphenyl	0.002	0.005	0.0125	0.025	0.0375	0.05	

Table 5. Column Degradation Evaluation Mix

Component	Concentration (µg/mL)
4,4'-DDT	0.040
Endrin	0.040

Table 6. LCS/Matrix Spike and Surrogate Spike Levels

Compound	(µg/L)	(µg/kg)
Aldrin	0.5	16.67
α-BHC	0.5	16.67
β-BHC	0.5	16.67
δ-BHC	0.5	16.67
γ-BHC (Lindane)	0.5	16.67
α-Chlordane	0.5	16.67
γ-Chlordane	0.5	16.67
4,4'-DDD	0.5	16.67
4,4'-DDE	0.5	16.67
4,4'-DDT	0.5	16.67
Dieldrin	0.5	16.67
Endosulfan I	0.5	16.67
Endosulfan II	0.5	16.67
Endosulfan Sulfate	0.5	16.67
Endrin	0.5	16.67
Endrin Aldehyde	0.5	16.67
Endrin Ketone	0.5	16.67
Heptachlor	0.5	16.67
Heptachlor Epoxide	0.5	16.67
Methoxychlor	0.5	16.67
Toxaphene (when required)	2.0	66.68
Surrogates		
Decachlorobiphenyl	0.2	6.67
Tetrachloro-*m*-xylene (TCMX)	0.2	6.67

Table 7. Evaluation Criteria and Corrective Actions for Continuing Calibration Verification

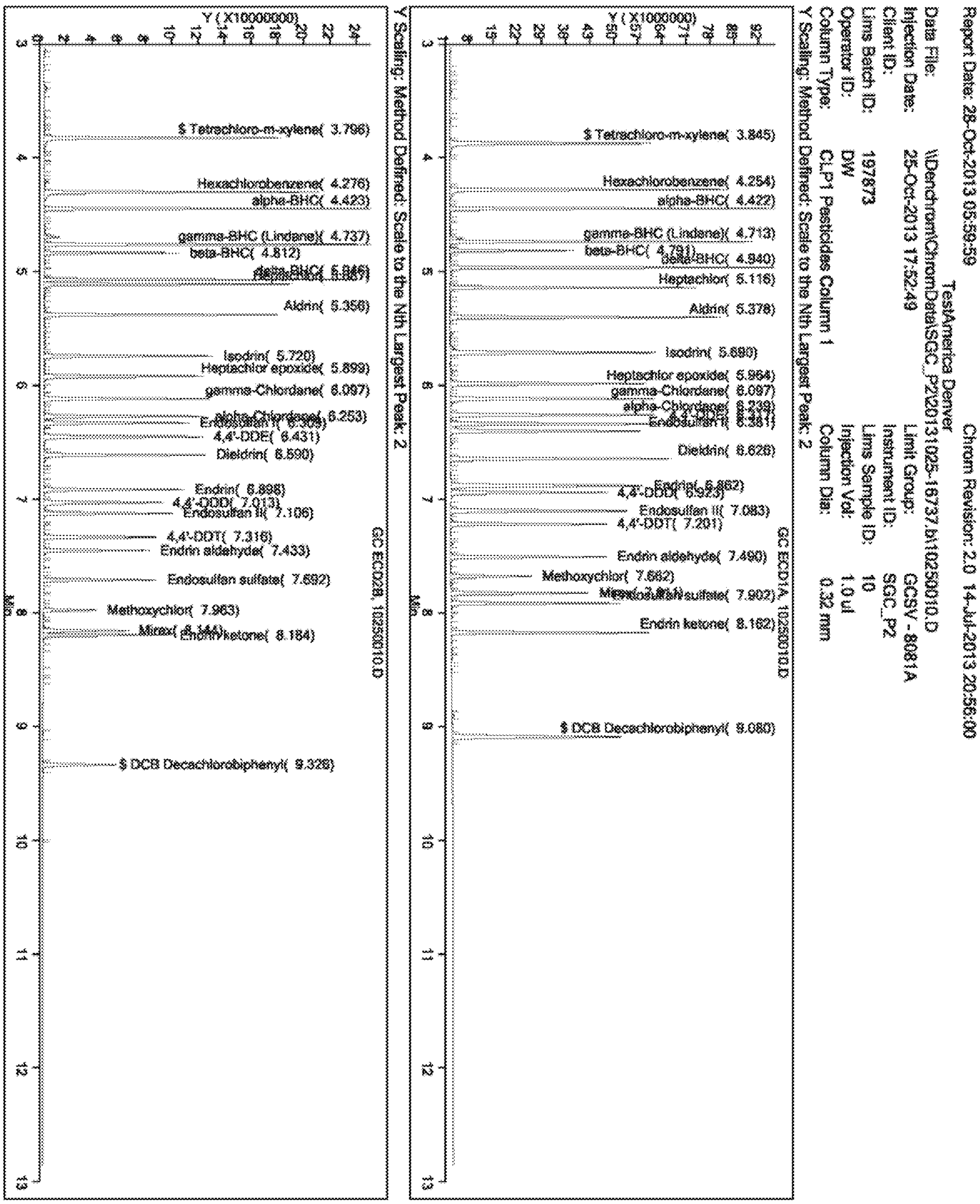
Evaluation Criteria for a Specific Analyte				Evaluation / Corrective Actions
Average %D	**Individual %D**	**RL Standard**	**Client Samples**	
N/A	± 15%	N/A	≥ RL	Calibration is verified for the analyte(s) detected in the sample; no action required.
N/A	Outside of ± 15%	N/A	≥ RL	Calibration is not verified for the analyte(s) detected in the sample. The sample must be re-analyzed using a verified calibration.
± 15%	± 30%	N/A	ND	Calibration is acceptable because analytes were not detected in the sample. An NCM is required.
Outside of ± 15%	N/A	N/A	N/A	Calibration is <u>not</u> verified and corrective action must be taken. NOTE: The exception to this may be those cases where the client has requested a small subset of the analytes typically measured by the method and the %D for each of those analytes is within ± 15%. Corrective action may include clipping the column, changing the liner, or other minor instrument adjustments, followed by reanalyzing the standard twice. If both results pass acceptance criteria, the calibration may be used to process samples. If the overall average %D still varies by more than ±15%, a new calibration curve must be prepared. Reanalyze any samples that were either preceded by or followed by the failed CCV using a verified calibration.
± 15%	< -30% (low)	Detected	ND	Sample results are acceptable because the RL standard indicates that the analyte would have been detected if present in the sample. Explain in an NCM.
± 15%	< -30% (low)	ND	ND	Analyte was not detected in the RL standard, possibly as the result of a calibration drift in the negative direction, and therefore one cannot be sure that the analyte would have been detected in the sample if present. Reanalyze samples with verified calibration.
± 15%	> +30% (high)	N/A	ND	Sample results are acceptable because the CCV failed high, so if the analyte were present in the sample, it would definitely have been detected. Explain in an NCM.

Note: Some programs (e.g., South Carolina) do not allow the average percent difference to be used in evaluating calibration verification standards. Please see the QAS's in the public folders for the current requirements.

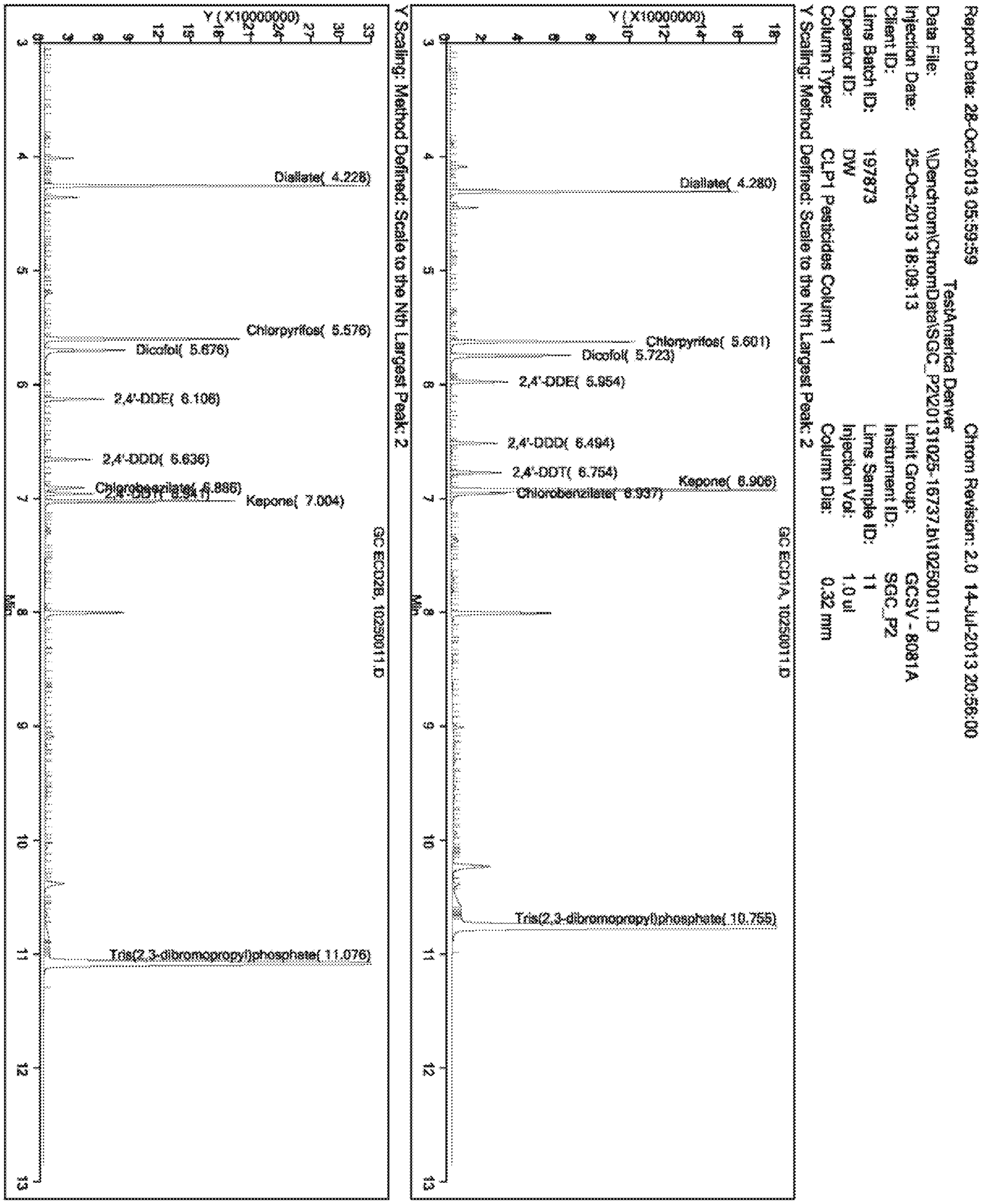
Table 8
Chrom Peak number assignment for analytes

Peak Number	Analyte
7	Tetrachloro-m-xylene
8	Hexachlorobenzene
9	Diallate
10	alpha-BHC
11	gamma-BHC (Lindane)
12	beta-BHC
13	delta-BHC
14	Chlordane (Technical)
15	Heptachlor
16	Aldrin
17	Chloropyrifos
18	Isodrin
19	Dicofol
20	Toxaphene
21	2,4'-DDE
22	Heptachlor Epoxide
23	gamma-Chlordane
24	alpha-Chlordane
25	4,4'-DDE
26	Endosulfan I
27	2,4'-DDD
28	Dieldrin
29	2,4'-DDT
30	Endrin
31	Kepone
32	4,4'-DDD
33	Chlorobenzilate
34	Endosulfan II
35	4,4'DDT
36	Endrin aldehyde
37	Methoxychlor
38	Mirex
39	Endosulfan sulfate
40	Endrin ketone
41	Propachlor
$41	Decachlorobiphenyl
42	Tris(2,3-dibromopropyl)phosphate

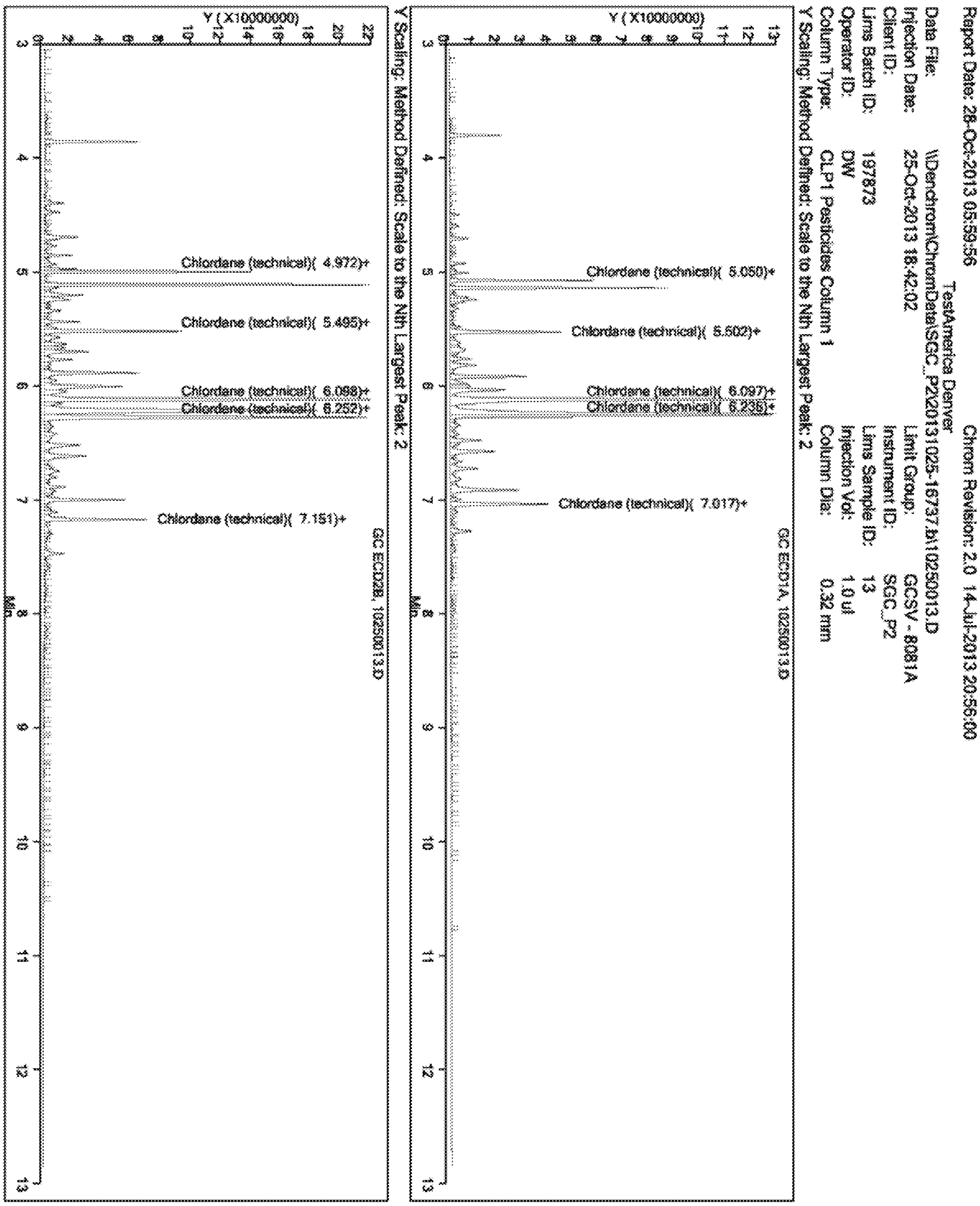
Attachment 1
Example Chromatogram – AB Standard



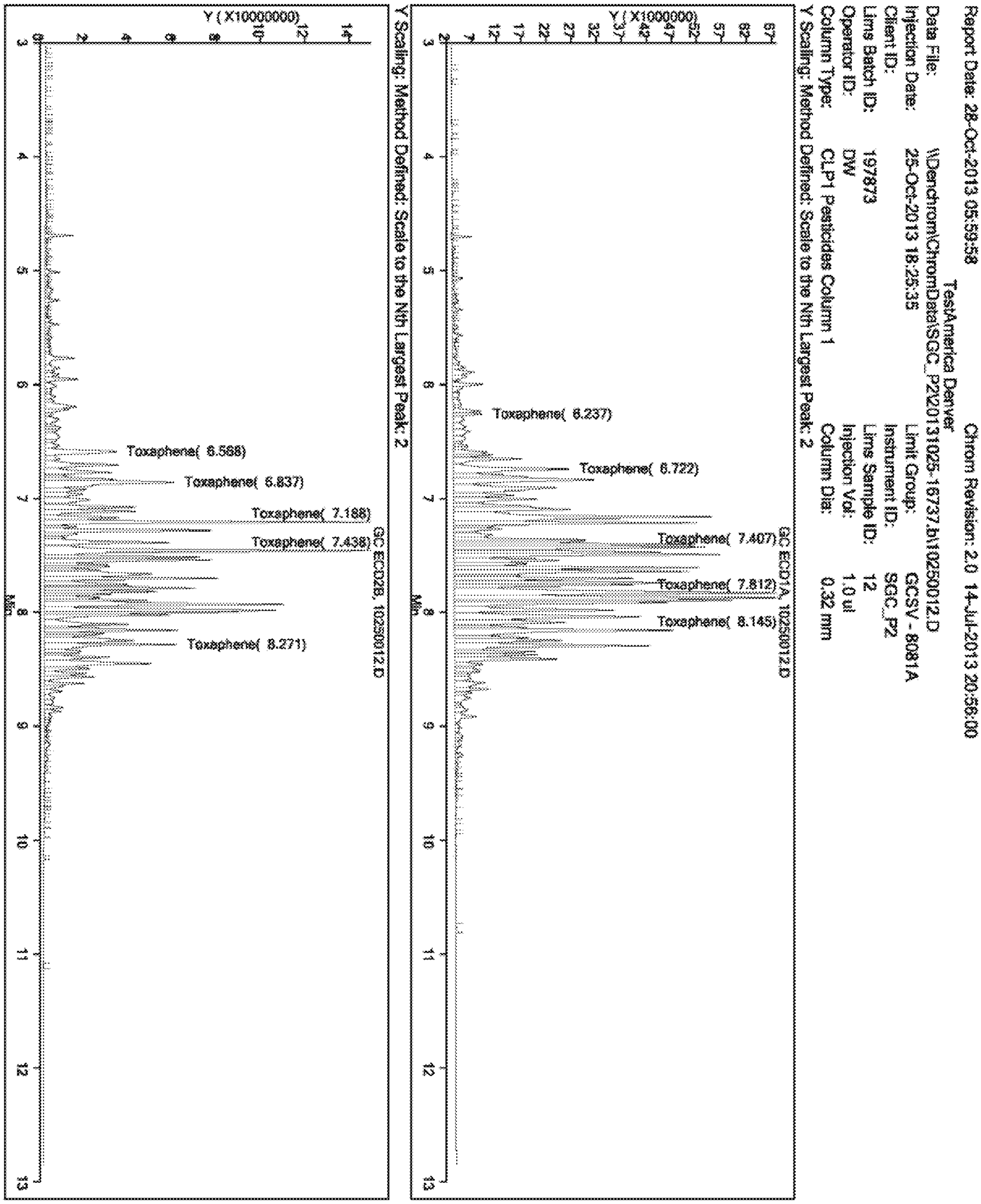
Attachment 2
Example Chromatogram – AP9 Standard



Attachment 3
Example Chromatogram – Chlordane (Technical)

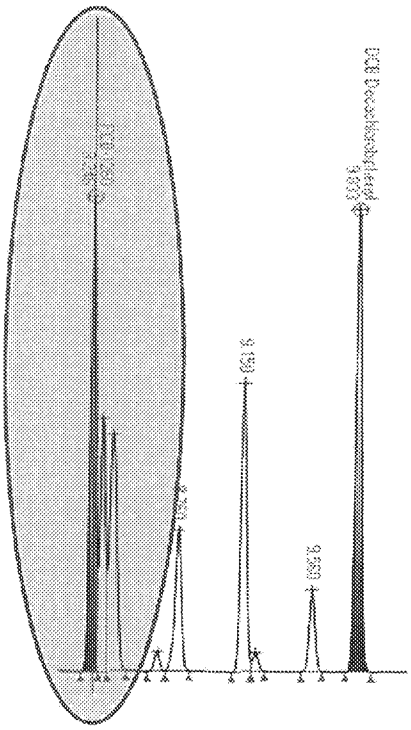


Attachment 4
Example Chromatogram – Toxaphene



Attachment 2.
Example of Minimum Resolution Requirement for Arochlor 1260 Triplet

(See Work Instruction CA-T-WI-003 for more information)



The circled triplet of peaks is observed towards the end of the 1260 pattern on columns such as CLP 1. Minimum resolution (degree of overlap) requirement between peak 1 / 2 and peak 2 / 3 is <75%. This chromatogram shows overlap of about 50% between peak 2 and 3, and 30% between peak 1 and 2.

Resolution (degree of overlap) is calculated as

[Height of the valley / (Sum of the two peak heights / 2)] x 100%

Work Instruction No. CA-T-WI-003, dated 31 Mar 2015

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Electronic Copy Only

Title: Extraction of Aqueous Samples by Separatory Funnel, SW846 3510C and EPA 600 Series

Approvals (Signature/Date):

Susan H. Oster 8/28/14	Adam W Alban 28 Aug 14
Susan Oster Date	Adam Alban Date
Organic Extractions Manager	Health & Safety Manager / Coordinator
Marie Fay for Margaret Sleevi 8/28/14	8/28/14
Margaret S. Sleevi Date	William S. Cicero Date
Quality Assurance Manager	Laboratory Director

Facility Distribution No. ____________ **Distributed To:**________________________

1.0 Scope and Application

This Standard Operating Procedure (SOP) is applicable to the solvent extraction of organic compounds from water samples, TCLP leachates, SPLP leachates, and Wyoming Leachates using a separatory funnel. This SOP based on SW-846 Method 3510C, EPA 608, EPA 610, EPA 614, AK102, NWTPH-Dx, and Oklahoma DRO method.

The determinative methods used in conjunction with this procedure are listed in Table 1. This extraction procedure may be used for additional methods when appropriate pH and spiking mixtures are used.

This procedure does not include the concentration and cleanup steps. See SOP DV-OP-0007, "Concentration of Organic Extracts", for details concerning the concentration and cleanup of extracts.

2.0 Summary of Method

A measured volume of sample, is placed in a separatory funnel. The pH is adjusted as required for the efficient extraction of specific compounds. The organic compounds are extracted with three portions of methylene chloride. The water phase is discarded. The organic phase is dried using sodium sulfate.

NOTE: The LVI procedure must not be used with samples from South Carolina at this time.

3.0 Definitions

3.1 **Extraction Holding Time**: The elapsed time expressed in days from the date of sample collection to the date the extraction starts. The holding time is tracked in the laboratory LIMS system, and is the primary basis of prioritizing work.

3.2 **Preparation Batch**: A group of up to 20 samples that are of the same matrix and are processed together in the same extraction event using the same procedure and lots of reagents and standards

3.3 **Method Comments:** The Method Comments are used to communicate to the bench level chemists special requirements and instructions from the client. Please reference WI-DV-0032 for details on Method Comments.

3.4 **Quality Assurance Summary (QAS)**: Certain clients may require extensive specific project instructions or program QC, which are too lengthy to fit conveniently in the Method Comments field in LIMS. In these situations, laboratory Project Managers describe the special requirements in a written QAS to address these requirements. QASs are posted on a public drive for easy accessibility by all lab employees. Normally, QASs are introduced to analysts in an initial project kick-off meeting to be sure that the requirements are understood.

3.5 **Aliquot**: A part that is a definite fraction of a whole; as in "take an aliquot of a sample for testing or analysis." In the context of this SOP, "aliquot" is also used as a verb, meaning to take all or part of a sample for preparation, extraction, and/or analysis.

4.0 Interferences

4.1 Chemical and physical interferences may be encountered when analyzing samples using this method.

4.2 Method interferences may be caused by contaminants in solvents, reagents, glassware, and other processing apparatus that lead to discrete artifacts. All these materials must be routinely demonstrated to be free from interferences under conditions of the analysis by running laboratory method blanks as described in the Quality Control section. Specific selection of reagents may be required to avoid introduction of contaminants.

4.3 Visual interferences or anomalies (such as foaming, emulsions, odor, etc.) must be documented in an NCM.

4.4 The most common interference is laboratory contamination, which may arise from impure reagents, dirty glassware, improper sample transfers, dirty work areas, etc. Be aware of potential sources of contamination and take appropriate measures to minimize or avoid them. Especially take note of the possibility of phthalate contamination from gloves. Gloves should be changed out frequently and whenever they come in contact with solvent. Glassware should be handled in a fashion that keeps gloves away from the interior and mouth of the glassware.

4.5 The decomposition of some analytes has been demonstrated under basic extraction conditions. Organochlorine pesticides may dechlorinate, phthalate esters may exchange, and phenol may react to form tannates. These reactions increase with increasing pH, and are decreased by the shorter reaction times available in Method 3510C. Method 3510C is preferred over Method 3520C for the analysis of these classes of compounds. However, the recovery of phenols is optimized by using Method 3520C and performing the initial extraction at the acid pH.

5.0 Safety

Employees must abide by the policies and procedures in the Environmental Health and Safety Manual, Radiation Safety Manual and this document.

This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, nitrile or latex gloves, lab coats and closed-toe, nonabsorbent shoes are a minimum.

5.1 Specific Safety Concerns or Requirements

5.1.1 The use of separatory funnels to extract samples using methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the separatory funnel has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity. Either a face shield must be worn over safety glasses or goggles must be worn when it is performed.

5.1.2 Glass centrifuge tubes can break in the centrifuge if proper care is not taken. This can lead to a hazardous material spill and endanger employees. Do not exceed the manufacturer's recommended maximum RPM for glass containers. Normally speeds greater than 2700 rpm are not advisable.

5.1.3 The procedure calls for the use of an electric rotator. The rotator is equipped with a safety latch that does not allow the rotator to rotate even if the power switch is turned on. The separatory funnels are secured to the rotator using straps. During the procedure it will be necessary to loosen the straps in order to un-stopper the separatory funnels. Whenever the straps are loose, the safety latch must be fastened to prevent the rotator from rotating.

5.1.4 Glasswool is a carcinogen and therefore should be handled in a hood to avoid inhalation of dust.

5.2 Primary Materials Used

The following is a list of the materials used in this method, which have a serious or significant hazard rating. **Note: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the MSDS for each of the materials listed in the table.** A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the MSDS for each material before using it for the first time or when there are major changes to the MSDS.

Materials with Serious or Significant Hazard Rating

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Methylene Chloride	Carcinogen Irritant	25 ppm (TWA) 125 ppm (STEL)	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting, and headache. Causes irritation, redness, and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Sodium Hydroxide	Corrosive Poison	2 mg/m3	Effects from inhalation of dust or mist vary from mild irritation to serious damage of the upper respiratory tract, depending on severity of exposure. Symptoms may include sneezing, sore throat, and runny nose. Contact with skin can cause irritation or severe burns and scarring with greater exposures. Causes irritation of eyes and can cause burns that may result in permanent impairment of vision, even blindness with greater exposures.

Material (1)	Hazards	Exposure Limit (2)	Signs and Symptoms of Exposure
Hydrochloric Acid	Corrosive Poison	5 ppm (Ceiling)	Inhalation of vapors can cause coughing, choking, inflammation of the nose, throat, and upper respiratory tract, and in severe cases, pulmonary edema, circulatory failure, and death. Can cause redness, pain, and severe skin burns. Vapors are irritating and may cause damage to the eyes. Contact may cause severe burns and permanent eye damage.
Sulfuric Acid	Corrosive Carcinogen	1 mg/m3	Inhalation may cause irritation of the respiratory tract with burning pain the nose and throat, coughing, wheezing, shortness of breath, and pulmonary edema. Causes chemical burns to the respiratory tract. Inhalation may be fatal as a result of spasm, inflammation, edema of the larynx and bronchi, chemical pneumonitis, and pulmonary edema. Causes skin burns. Causes severe eye burns. May cause irreversible eye injury, blindness, permanent corneal opacification.
(1) Always add acid to water to prevent violent reactions. (2) Exposure limit refers to the OSHA regulatory exposure limit			

6.0 Equipment and Supplies

NOTE: All glassware used in this procedure is cleaned following SOP DV-OP-0004. In addition, the glassware is rinsed with methylene chloride immediately prior to use.

6.1 Supplies

- Separatory funnel, 2-liter with polytetrafluoroethylene (PTFE) stopcock and stopper.
- Separatory funnel, 500-mL with polytetrafluoroethylene (PTFE) stopcock and stopper.
- Separatory funnel rack and mechanical rotator.
- Balance, ≥ 1400 g capacity, accurate to ± 1 g, calibration checked daily per SOP DV-QA-0014.
- pH indicator paper, wide range.
- Class A Graduated Cylinder, sizes ranging from 50 mL to 1 L.
- Media bottles, 300 mL with Teflon-lined caps or capped with aluminum foil.
- Media bottles, 100 mL with Teflon-lined caps or capped with aluminum foil.
- Disposable pipettes, various volumes.
- Stemless glass funnel.
- Glass wool, baked at 400 ϒC for four hours.
- Mechanical pipette, 1 mL, positive displacement, with disposable tips, calibrated per SOP DV-QA-0008.
- Aluminum foil.
- Paper towels.

6.2 Computer Software and Hardware

Please refer to the master list of documents, software and hardware located on G:\QA\Read\Master List of Documents\Master List of Documents, Software and Hardware.xls or current revision for the current software and hardware to be used for data processing.

7.0 Reagents and Standards

Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.1 Reagent Water

7.1.1 TestAmerica Denver has two ELGA water purification systems. The water coming from the ELGA system should be 18-18.2 Mohm-cm. The performance of the water polishing system is checked daily and recorded per SOP DV-QA-0026.

7.2 Methylene Chloride

Each lot of solvent is tested following SOP CA-Q-S-001 DV-1 before it is put into use. QA personnel post the list of approved lots at solvent storage areas.

7.3 Acids and Bases

7.3.1 Sulfuric Acid (H2SO4), 1:1
TALS Reagent ID "1:1 H2SO4"

Place an ice water bath on a stir plate. Place a container with a magnetic stir bar in the bath. While stirring, slowly add 1 part concentrated reagent grade sulfuric acid (36N) to 1 part water from the ELGA purification system. Assign a 1 year expiration date from the date made or the vender expiration date, whichever is shorter.

7.3.2 Sodium Hydroxide (NaOH), 10N
TALS Reagent ID "10N_NaOH"

Purchased at ready-to-use concentration from commercial vendors. Assign a 1 year expiration date from the date opened or the vender expiration date, whichever is shorter.

7.3.3 Hydrochloric Acid (HCl), 1N
TALS Reagent ID "1N_HCl"

Dilute 100 mL of stock reagent grade, concentrated HCl to 1000 mL with reagent water.

7.4 Baked Sodium Sulfate, 12-60 mesh

Heat sodium sulfate in a 400 ℃ oven for at least four hours. Store in tightly closed container.

7.5 Baked Sodium Chloride

Bake in 400 ℃ oven for at least 4 hours.

Standards

7.6 Please reference SOP DV-OP-00020 and WI-DV-009 for information regarding the surrogate and spike standards used in this procedure.

8.0 Sample Collection, Preservation, Shipment and Storage

Sample container, preservation techniques and holding times may vary and are dependent on sample matrix, method of choice, regulatory compliance, and/or specific contract or client requests. Listed below are the holding times and the references that include preservation requirements.

Matrix and Method	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Water	Amber Glass	1000 mL	Cool, $\leq 6^{o}C$	7 Days	40 CFR Part 136.3
Water for Method AK 102	Amber Glass	1000 mL	Cool, $\leq 6^{o}C$ and pH ≤ 2 with HCl	14 Days if properly preserved. 7 Days if un-preserved.	Method AK 102
Water for Method Oklahoma DRO	Amber Glass	1000 mL	Cool, $\leq 6^{o}C$ and pH ≤ 2 with HCl	7 Days	Oklahoma Dept. of Environmental Quality
Water for Method NWTPH-DX	Amber Glass	1000 mL	Cool, $\leq 6^{o}C$ and pH ≤ 2 with HCl	7 Days	NWTPH-Dx
Water for Method 8082 or 8082A	Amber Glass	1000 mL	Cool, $\leq 6^{o}C$	None [2]	SW-846 Chapter 4, Revision 4, Feb 2007
Water for Method 8081 or 8082 by Large Volume Injection	Amber Glass	250 mL	Cool, $\leq 6^{o}C$	7 Days	40 CFR Part 136.3
Water for Method 8270 by Large Volume Injection	Amber Glass	250 mL	Cool, $\leq 6^{o}C$	7 Days	40 CFR Part 136.3
TCLP Leachates	Glass	200 mL for 8270 100 mL for 8081	Cool, $\leq 6^{o}C$	7 Days from the start of the leach	SW-846 1311
SPLP Leachates	Glass	1000 mL	Cool, $\leq 6^{o}C$	7 Days from the start of the leach	SW-846 1312

Matrix and Method	Sample Container	Min. Sample Size	Preservation	Holding Time [1]	Reference
Wyoming Leachates	Glass	1000mL	Cool, $\leq 6^{o}C$	7 Days from the start of the leach	--

[1] Exclusive of analysis.
[2] Some regulatory agencies do not accept SW-846 Revision 4 of Chapter 4 and will require a 1 week hold time for method 8082 and 8082A. The states of California, South Carolina, Pennsylvania, and Connecticut require a 1 week hold time.

9.0 Quality Control

9.1 The minimum quality controls (QC), acceptance criteria, and corrective actions are described in this section. When processing samples in the laboratory, use the LIMS Method Comments to determine specific QC requirements that apply.

9.1.1 The laboratory's standard QC requirements, the process of establishing control limits, and the use of control charts are described more completely in TestAmerica Denver policy DV-QA-003P, Quality Assurance Program.

9.1.2 Specific QC requirements for Federal programs, e.g., Department of Defense (DoD), Department of Energy (DOE), AFCEE, etc., are described in TestAmerica Denver policy DV-QA-024P, Requirements for Federal Programs. This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated.

9.1.3 Project-specific requirements can override the requirements presented in this section when there is a written agreement between the laboratory and the client, and the source of those requirements should be described in the project documents. Project-specific requirements are communicated to the analyst via Method Comments in the LIMS and the Quality Assurance Summaries (QAS) in the public folders.

9.1.4 Any QC result that fails to meet control criteria must be documented in a Nonconformance Memo (NCM). The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP DV-QA-0031. This is in addition to the corrective actions described in the following sections.

9.2 Initial Performance Studies

Before analyzing samples, the laboratory must establish a method detection limit (MDL). In addition, an initial demonstration of capability (IDOC) must be performed by each analyst on the instrument he/she will be using. On-going proficiency must be demonstrated by each analyst on an annual basis. See Section 13 for more details on detection limit studies, initial demonstrations of capability, and analyst training and qualification.

9.3 Batch Definition

Batches are defined at the sample preparation stage. The batch is a set of up to 20 samples of the same matrix, plus required QC samples, processed using the same procedures and reagents within the same time period. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. The method blank must be run on each instrument that is used to analyze samples from the same preparation batch. See QC Policy DV-QA-003P for further details.

9.4 Method Blank (MB)

At least one method blank must be processed with each preparation batch. The method blank is processed and analyzed just as if it were a field sample.

The method blank for batches of aqueous samples for Large Volume Injection (prep method 3510C_LVI) consists of 250mL of reagent water free of any of the analyte(s) of interest.

The method blank for batches of aqueous samples for all other methods consists of 1 L of reagent water free of any of the analyte(s) of interest.

The method blank for batches of TCLP leachates for method 8081 consists of 100 mL of leach fluid.

The method blank for batches of TCLP leachates for method 8270 consists of 200 mL of leach fluid.

The method blank for batches of SPLP or Wyoming leachates consists of 1 L of leach fluid.

9.5 Laboratory Control Sample / Laboratory Control Sample Duplicate (LCS/LCSD)

At least one LCS must be processed with each preparation batch. The LCS is carried through the entire analytical procedure just as if it were a sample.

The LCS for batches of aqueous samples for Large Volume Injection (prep method 3510C_LVI) consists of 250mL of reagent water to which the analyte(s) of interest are added at known concentrations.

For aqueous sample batches for all other methods, the LCS consists of 1 L of reagent water to which the analyte(s) of interest are added at known concentration.

For method 8081 TCLP leachates, the LCS consists of 100 mL of leach fluid to which the analyte(s) of interest are added at known concentration.

For method 8270 TCLP leachates, the LCS consists of 200 mL of leach fluid to which the analyte(s) of interest are added at known concentration.

For SPLP leachates and Wyoming leachates, the LCS consists of 1 L of leach fluid to which the analyte(s) of interest are added at known concentration.

Method 608, 614, 610 requires a LCS at a 10% frequency. In other words one LCS is required for a batch of 10 or less samples. A LCSD is required for a batch of 11 or more samples.

Method AK102 requires LCS and a LCSD for every batch for every spike compound.

9.6 Matrix Spike/Matrix Spike Duplicate (MS/MSD)

One MS/MSD pair must be processed with each preparation batch. A matrix spike (MS) is a field sample to which known concentrations of target analytes have been added. It is prepared in a manner similar to the LCS, but uses a real sample matrix in place of the blank matrix. A matrix spike duplicate (MSD) is a second aliquot of the same sample (spiked exactly as the MS) that is prepared and analyzed along with the sample and matrix spike. Some programs allow spikes to be reported for project-related samples only. Samples identified as field blanks cannot be used for the MS/MSD analysis.

If insufficient sample volume is available for MS/MSD, an NCM must be written and a LCSD must be prepared unless Method Comments indicate otherwise.

Method 608, 610, and 614 requires one matrix spike for every 10 samples. If the batch has more than 10 samples, then two matrix spikes must be performed. The two matrix spikes are to be performed on two different samples. If there is insufficient sample volume for matrix spikes, then a LCSD must be performed.

Method NWTPH-Dx requires a matrix spike and a matrix spike duplicate for every 10 samples. If insufficient sample volume is available for MS/MSD, a NCM must be written and a LCS and LCSD must be performed for every 10 samples.

9.7 Surrogate Spikes

Every calibration standard, field sample, and QC sample (i.e. method blank, LCS, LCSD, MS, and MSD) is spiked with surrogate compounds.

10.0 Procedure

10.1 One-time procedural variations are allowed only if deemed necessary in the professional judgment of supervision to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using an NCM. The NCM is automatically sent to the laboratory Project Manager by e-mail so that the client can be notified as appropriate. The QA group periodically reviews NCMs for potential trends. The NCM process is described in more detail in SOP # DV-QA-0031. The NCM shall be filed in the project file and addressed in the case narrative. Any deviations from this procedure identified after the work has been completed must be documented in an NCM, with a cause and corrective action described.

10.2 Critical Procedural Considerations

10.2.1 As stated throughout this SOP, analysts must review the Method Comments and any applicable QASs before starting work. This review is also documented on the Organic Extraction Checklist (see WI-DV-0009).

10.2.2 Analyst must focus on using clean technique throughout this procedure. Any parts or pipettes that come into direct contact with dirty surfaces or any other separatory funnel than the designated one should be cleaned or disposed of before coming into contact with the sample.

10.3 Assemble and clean the glassware immediately before use.

10.3.1 Place a stopcock in each separatory funnel. For 1-liter extractions use a 2000mL sepfunnel. For 250mL, 200mL and 100mL extractions, use a 500mL sepfunnel. Place a stopper for each separatory funnel on a clean sheet of aluminum foil that is marked with individual positions for each stopper. This is done to prevent cross-contamination.

NOTE: Samples logged with method 3510_LVI are for Large Volume Injection methods and require 250mL initial volumes. Samples logged for 8270 with a TCLP pre-prep require 200mL initial volumes. Samples logged for 8081 with a TCLP pre-prep require 100mL initial volumes.

10.3.2 For each separatory funnel, plug a glass funnel with baked glass wool and add baked sodium sulfate. Place the funnel on a media bottle and place the media bottle below the separatory funnel.

10.3.3 Rinse each separatory funnel once with methylene chloride. Be sure that all surfaces come into contact with the solvent. Drain the methylene chloride into the media bottle through the sodium sulfate.

10.3.4 Rinse the sodium sulfate with additional methylene chloride if the first rinse did not completely saturate the sodium sulfate.

10.3.5 Allow the methylene chloride to drain completely into the media bottle. Swirl the media bottle to ensure all surfaces come into contact with the solvent. Add additional methylene chloride to the rinse if necessary.

10.3.6 Discard the methylene chloride.

10.3.7 Label each media bottle with the sample ID or batch QC ID.

10.4 Prepare LCS and Method Blank Samples

NOTE: For SW-846 methods if there is not a MS/MSD pair in the batch then perform a LCS/LCSD. Methods 608, 610, and 614 require a LCS and LCSD in batches of 11 samples or more or if there are no Matrix Spikes in batches of 10 or less.

10.4.1 For aqueous sample batches logged for Large Volume Injection, (3510_LVI), pour 250mL of reagent water into the separatory funnels marked for the LCSs and the MB.

10.4.2 For all other aqueous sample batches, pour 1 liter of reagent water into the separatory funnels marked for the LCSs and the MB.

10.4.3 For 8270 TCLP leachates, use a 250mL or 500mL Class A graduated cylinder to measure out 200 mL of the appropriate leach fluid for each MB and LCS and LCSD. Record the volume to the nearest mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct leach fluid was used.

10.4.4 For 8081 TCLP leachates, use a 100mL or 250mL Class A graduated cylinder to measure out 100 mL of the appropriate leach fluid for each MB and LCS and LCSD. Record the volume to the nearest mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct leach fluid was used.

10.4.5 For SPLP leachates, use a 1000mL Class A graduated cylinder to measure out 1000 mL of the appropriate leach fluid for each MB and LCS and LCSD. Record the volume to the nearest 10 mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct leach fluid was used.

10.4.6 For Wyoming leachates, measure out 1000 mL of the appropriate leach fluid for each MB and LCS and LCSD. This can be done gravimetrically or volumetrically. If done volumetrically, record the volume to the nearest 10mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct blank fluid was used.

10.5 Measure the initial sample pH of the samples.

10.5.1 Measure the initial sample pH with wide-range pH paper and record the pH on the extraction bench sheet.

10.5.2 If the sample is logged for AK102_103, Okla_DRO, or NWTPH_Dx the samples should have been field preserved. See Section 8. If the samples are not preserved, an NCM should be written.

10.6 Aliquot the samples

10.6.1 For 8270 TCLP leachates, use a 250mL or 500mL Class A graduated cylinder to measure out 200 mL of the leachate. Record the volume to the nearest mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct leach fluid was used.

10.6.2 For 8081 TCLP leachates, use a 100mL or 250mL Class A graduated cylinder to measure out 100 mL of the leachate. Record the volume to the nearest mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct leach fluid was used.

10.6.3 For SPLP leachates, use a 1 Liter Class A graduated cylinder to measure out 1000 mL of the leachate. Record the volume to the nearest 10 mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct leach fluid was used.

10.6.4 For Wyoming leachates, measure out 1000 mL of leachate. This can be done gravimetrically or volumetrically. If done volumetrically, use a Class A graduated cylinder and record the volume to the nearest 10mL. Place the leachate bottle beside the separatory funnel so a second analyst can check that the correct blank fluid was used.

10.6.5 For water samples, it should be noted that TestAmerica Denver routinely aliquots gravimetrically. This is done to prevent cross-contamination due to volumetric glassware and to provide a more accurate initial volume measurement. However, some clients and regulatory programs require the laboratory to aliquot samples volumetrically. The Method Comments and QASs must be read before samples are aliquotted to check for this requirement. If samples are to be aliquotted volumetrically, use Class A volumetric glassware only and proceed to Section 10.6.7

10.6.6 Weigh the bottle (250mL amber bottles for 3510C_LVI or 1000mL amber bottles for all other aqueous samples) and record the gross weight to the nearest gram. If there is any indication that the sample's density is not 1g=1mL, then measure the density of the sample using a calibrated pipette and an analytical balance. The weight of the sample extraction will be corrected for the density later. See Section 11 for the calculation. For example, normally a 1 liter bottle weighs 500g when empty and when filled completely can only hold 1060mL, therefore a full bottle weighing more than 1560g is an indication that either the sample density is greater than 1g or the sample bottle contains a lot of sediment. Document any sample with a density greater than 1g in an NCM.

10.6.7 Inspect the samples for large amounts of sediment that may interfere with the extraction of the sample by causing excessive emulsions or clogging the stop-cock.

10.6.7.1 If the sample contains so much sediment that the entire sample volume cannot be extracted, decant the sample into the separatory funnel (or a 1 L graduated cylinder if volumetric aliquotting is required), careful not to transfer the sediment. Write a NCM to document the sediment and that it prevented the entire sample volume from being extracted and the sample container from being solvent rinsed.

10.6.7.2 If the sample does not contain a significant amount of sediment, then the entire sample volume will be used in the extraction. Do not pour the sample into the separatory funnel (or into the graduated cylinder if volumetric aliquotting is required) until after the surrogates and any necessary spikes have been added to the samples.

10.6.8 Place the sample containers in front of the separatory funnel labeled for that sample. A second analyst should then check the labels to make sure the correct sample is being extracted. This check is documented in the Organic Extraction Checklist (WI-DV-0009)

10.7 Add Surrogates to All Field Samples and QC Samples

10.7.1 The standards should be allowed to come to room temperature before spiking the samples. Record the ID of the standard used on the benchsheet.

NOTE: The addition of spikes and surrogates to samples must be done only immediately after a second analyst has reviewed the batch. Reference work instruction WI-DV-009.

10.7.2 Only one batch should be surrogated at a time to ensure the correct standards are used.

10.7.3 Add the appropriate volume of the appropriate working surrogate standard to the sample container for each sample and MS/MSD. Add the surrogate standard to the MB and the LCS's in the separatory funnels. Record the ID of the standard used on the bench sheet. Reference work instruction WI-DV-009 to determine the appropriate standard and the appropriate volume.

Note: If the sample contains an amount of sediment that has been deemed to interfere with the extraction process then the surrogate standard is added to the sample in the separatory funnel or in the graduated cylinder. This is considered a deviation and must be documented in a NCM.

10.8 Add Spikes to all LCS's and MS/MSDs

10.8.1 Add the appropriate volume of the appropriate working spike standard to the MS/MSD sample containers and the separatory funnels for the LCS and/or LCSD samples. Record the ID of the standard used on the bench sheet. Reference work instruction WI-DV-009 to determine the appropriate standard and the appropriate volume.

10.9 Add approximately 6g (1 teaspoon) of NaCl to all samples and all QC samples. This is done to give the reagent water used in the MBs and LCSs some ionic strength to more closely mimic the matrix of actual water samples and to aide in the extraction of the more polar target compounds. Record the lot number of the sodium chloride on the bench sheet.

NOTE: South Carolina samples must be batched separately. QC samples for these batches use reagent water directly from the Elga system. ***DO NOT ADD NaCl to any South Carolina samples or QC samples.***

10.10 If volumetric aliquotting is required, transfer the entire sample into a Class A graduated cylinder and record the volume on the benchsheet. If the sample bottle contains more than 1000 mL, a 100mL Class A graduated cylinder can be used to complete the measurement. The entire sample volume must be used. Record the volume to the nearest 10 mL. Then pour the sample into the labeled separatory funnel. Place the used graduated cylinder in front of the appropriate separatory funnel so it can be solvent rinsed later.

NOTE: A 1000 mL Class A graduated cylinder is not accurate enough to measure to the nearest 1 mL. Therefore all samples that are aliquoted using a 1000 mL Class A graduated cylinder will have the initial volume recorded to the nearest 10 mL. This accuracy is sufficient.

10.11 If volumetric aliquotting is not required, pour the sample directly into the separatory funnel. Place the empty sample container in front of the appropriate separatory funnel so it can be solvent rinsed.

10.12 Adjust pH of Field Samples and QC Samples

Adjust the sample pH as indicated in the chart below using a minimum amount of 1:1 sulfuric acid (or 1 M hydrochloric acid for Methods AK102, Okla_DRO and NWTPH_Dx) or 10 N sodium hydroxide, as necessary. Record the adjusted pH and the lot number of the acid or base on the bench sheet.

NOTE: TCLP Leachates may have pH of < 5. In those cases, the pH should be adjusted per the table below.

Method	Initial Extraction pH	Secondary Extraction pH
All 8270 methods *except* SIM.	1 – 2	If samples are TCLP leachates extract at 14. If samples are water extract at 11 - 12
All 8270 SIM methods	As Received	None
All 8081, 8082 and 608 methods.	5 - 9	None
All 8141 and 614 methods	5-8	None
All 8015 methods	As Received	None
All 8310 and 610 methods	As Received	None
AK102_103 Okla_DRO NWTPH_Dx	If samples are preserved between pH 1 – 2, then acidify the MB and LCS. Otherwise extract as received and document insufficient preservation in an NCM.	None

10.13 For 1 Liter samples, add 60 mL of methylene chloride to each empty sample container, unless the entire sample volume was not used. For 250mL or smaller samples, add 30mL of methylene chloride to each empty sample container, unless the entire sample volume was not used. Cap the container and shake gently to rinse all internal surfaces of the bottle. Pour the methylene chloride from the sample container into the appropriate separatory funnel. If a graduated cylinder was used to aliquot volumetrically, rinse the cylinder and add that rinse to the separatory funnel as well. Record the lot number of the methylene chloride on the bench sheet. If the sample contained significant sediment and the entire sample contents could not be extracted, do not rinse the empty sample container, but instead add the solvent directly to the separatory funnel. If the solvent rinse of the sample container cannot be performed, prepare a NCM.

10.14 For water samples that were aliquotted gravimetrically, reweigh the bottle and calculate the initial sample volume by subtracting the empty bottles weight from the full bottles weight, assuming a density of 1g=1mL. If there is any indication that the samples density is not 1g=1mL then measure the density of the sample and correct the calculated initial volume accordingly using the formula in Section 11. Document abnormal sample density in an NCM. For example, normally a 1 liter bottle when filled completely can only hold 1060mL, therefore an initial volume greater than 1060mL is an indication that the density is not 1g. Document any sample with a density greater than 1g in an NCM.

10.15 If the initial volume is less than 80% of the nominal volume, the sample reporting limits and method detection limits will be elevated substantially. Document this in a NCM.

10.16 Stopper and rotate the separatory funnel for 3 minutes with periodic venting to release excess pressure. Document the extraction date and time on the benchsheet.

WARNING: Methylene chloride creates excessive pressure very rapidly! Therefore, initial venting should be done immediately after the separatory funnel has been sealed and shaken a few seconds. Vent into hood away from people and other samples. A face shield or goggles must be worn during venting.

10.17 Allow the organic layer to separate from the water phase for at least 5 minutes or until complete visible separation has been achieved. This can take up to 10 minutes. If the emulsion interface between layers is more than one-third the size of the solvent layer, use mechanical techniques to complete the phase separation. The optimum technique depends upon the sample and may include stirring, pouring the solvent layer and emulsion back through the top of the separatory funnel (pour-back), or centrifugation. The emulsion could also be filtered through the glass funnel by adding additional sodium sulfate to remove all water in the emulsion. This technique should only be used after other techniques have failed to make complete phase separation and only after the last shake.

NOTE: If an emulsion forms, the analyst does not have to wait a complete 5 minutes before attempting to break the emulsion with pour-backs and centrifuge. Start employing the mechanical techniques right away to achieve phase separation.

NOTE: As much as 15 to 20 mL of methylene chloride is expected to dissolve in 1 L of water. Thus, solvent recovery could be as low as 35 mL from the first shake and still be acceptable. Subsequent shakes should recover at least 50 mL of solvent.

10.18 Drain the lower methylene chloride layer into the sodium sulfate filled glass funnel. Allow the methylene chloride to drain completely into the media bottle. Rinse the sodium sulfate with a small amount of methylene chloride to ensure that all compounds of interest are collected in the media bottle. Record the lot number of the sodium sulfate on the bench sheet. If the sodium sulfate becomes saturated with water, add more to the funnel or replace the existing sodium sulfate with fresh drying agent.

10.19 Repeat the extraction two more times for a total of 3 extractions. Collect all three methylene chloride extracts in the same media bottle. For the 2^{nd} and 3^{rd} extractions it is not necessary to wait 5 minutes to allow the solvent to separate from the water; a 3 minute wait time should be sufficient.

10.20 For the base/neutral and acid extractable method 8270, adjust the pH of the samples according to chart in Section 10.12. For 8270 TCLP samples an excess of base is required to effectively extract pyridine, therefore more than 5mL of base should be used to ensure the pH is 14. Then extract the sample 3 more times. For these extractions, it is not necessary to wait 5 minutes to allow the solvent to separate from the water; a 3 minute wait time should be sufficient.

10.21 Cap the media bottle with a Teflon-lined cap or aluminum foil and submit for concentration and possible clean-up steps.

10.22 Dispose of the solvent-saturated water remaining in the separatory funnel in the appropriate waste container. See Section 14.

10.23 Initial weights and volumes of samples are entered into LIMS, and the transcribed data must be verified by a second person. This verification is documented on the Organic Extraction Checklists (see WI-DV-009).

10.24 Troubleshooting

10.24.1 If the sample appears very dark or viscous or in any way un-like water, stop and test the sample's miscibility before attempting to extract the sample by this procedure. Place a few milliliters of sample in a vial with methylene chloride. Cap and shake. If the sample is miscible in methylene chloride, the sample should be re-logged as a waste matrix with a prep method of 3580A.

10.25 Maintenance

10.25.1 Approximately every 6 months, the centrifuge should be lubricated.

10.25.2 Contact the Facilities Manager immediately if the rotator is observed to be making un-familiar noises or rotating in a "jerking" manner.

11.0 Data Analysis and Calculations

$$InitialVolume(mL) = \frac{FullBottle(g) - EmptyBottle(g)}{Density(g/mL)}$$

12.0 Method Performance

12.1 Before analyzing samples, the laboratory must establish a method detection limit (MDL). See Policy DV-QA-005P, "Determination of Method Detection Limits", for more information on the method detection limit studies.

12.2 An initial demonstration of capability (IDOC) must be performed by each analyst. On-going proficiency must be demonstrated by each analyst on an annual basis. See DV-QA-0024, "Employee Training", for more information on the IDOCs.

12.3 Training Qualification

The group/team leader has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience. Further details concerning the training program are described in SOP DV-QA-0024.

13.0 Pollution Control

The volume of spike solutions prepared is minimized to reduce the volume of expired standard solutions requiring hazardous waste disposal.

14.0 Waste Management

14.1 All waste will be disposed of in accordance with Federal, State, and local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment. Employees will abide by this procedure, the policies in section 13, "Waste Management and Pollution Prevention", of the Environmental Health and Safety Manual, and DV-HS-001P, "Waste Management Program."

14.2 The following waste streams are produced when this method is carried out:

14.2.1 Methylene chloride – Waste Stream B

14.2.2 Solid waste/sodium sulfate – Waste Stream D

14.2.3 Basic aqueous sample waste saturated with methylene chloride – Waste Stream X.

14.2.4 Acidic aqueous sample waste saturated with methylene chloride – Waste Stream Y.

14.2.5 Neutral aqueous sample waste saturated with methylene chloride – Waste Stream X or Waste Stream Y.

14.2.6 Expired Standards/Reagents – Contact Waste Coordinator for guidance

NOTE: Radioactive waste, mixed waste, and potentially radioactive waste must be segregated from non-radioactive waste as appropriate. Contact the Radioactive Waste Coordinator for proper management of these materials.

15.0 References / Cross-References

15.1 SW-846, Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Third Edition and all promulgated updates, EPA Office of Solid Waste, January 2005, Method 3510C, Separatory Funnel Liquid-Liquid Extraction, Revision 3, December 1996.

15.2 Code of Federal Regulations, Title 40 – Protection of the Environment, Part 136 – Guidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix A – Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Method 608, Organochlorine Pesticides and PCBs.

15.3 Code of Federal Regulations, Title 40 – Protection of the Environment, Part 136 – Guidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix A – Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, Method 610, Polynuclear Aromatic Hydrocarbons.

15.4 Code of Federal Regulations, Title 40 – Protection of the Environment, Part 136 – Guidelines Establishing Test Procedures for the Analysis of Pollutants, Appendix A – Methods for

Organic Chemical Analysis of Municipal and Industrial Wastewater, Method 614, Organophosphorous Pesticides.

15.5 Alaska Method AK102, "For the Determination of Diesel Range Organics", Version 04/08/02.

15.6 Alaska Method AK103, "For the Determination of Residual Range Organics", Version 04/08/02.

15.7 NWTPH-Dx "Semi-Volatile Petroleum Products Method for Soil and Water.

15.8 Oklahoma Department of Environmental Quality Methods 8000/8100 (Modified) Diesel Range Organics (DRO) Revision 4.1 Date 10/22/97

16.0 Modifications:

16.1 Modifications from SW-846 Method 3510C

16.1.1 Section 7.1 of the method calls for initial sample volume to be determined volumetrically either by measuring out exactly 1 liter or marking the meniscus on the sample container and later determining the volume of water required to fill the bottle back up to the mark. This SOP allows the initial sample volume to be determined by weight in order to achieve a more accurate initial volume and to avoid cross-contamination via glassware.

16.1.2 Section 7.5 of the method calls for shaking the separatory funnel 1-2 minutes. This SOP calls for shaking the separatory funnel for 3 minutes.

16.1.3 Section 7.6 of the method calls for allowing the organic layer to separate from the water phase for a minimum of 10 minutes. This SOP calls for allowing the organic layer to separate from the water phase for a minimum of 5 minutes after the first extraction and a minimum of 3 minutes for subsequent extractions, up to 10 minutes if the separation is not complete.

16.1.4 The source method does not call for the use of sodium chloride. This procedure calls for the addition of approximately 6g of sodium chloride to all samples and all QC samples in order to help the extraction efficiency.

16.1.5 The source method calls for samples to be extracted for method 8141 at the pH they are received. This procedure calls for the extraction to be performed at a pH between 5 and 8. This is done per guidelines found in Section 2 and Section 8 of SW-846 8141B.

16.2 Modifications from 40 CFR Method 608, and 610

16.2.1 Section 10.1 of the method calls for initial sample volume to be determined volumetrically. This SOP allows the initial sample volume to be determined by weight.

16.2.2 Section 10.2 of the method calls for shaking the separatory funnel 1-2 minutes. This SOP calls for shaking the separatory funnel for 3 minutes.

16.2.3 Section 10.2 of the method calls for allowing the organic layer to separate from the water phase for a minimum of 10 minutes. This SOP calls for allowing the organic layer to separate from the water phase for a minimum of 5 minutes after the first extraction and a minimum of 3 minutes for subsequent extractions, up to 10 minutes if the separation is not complete.

16.2.4 Section 10.3 of the method calls for rinsing the sample collection bottle with the 60 mL methylene chloride aliquot for the second and third extraction as well as the first extraction. This SOP calls for rinsing the sample collection bottle with only the first 60-mL methylene chloride aliquot.

16.2.5 The source method does not call for the use of sodium chloride. This procedure calls for the addition of approximately 6g of sodium chloride to all samples and all QC samples in order to help the extraction efficiency.

16.3 Modifications from 40 CFR Method 614

16.3.1 Section 10.1 of the method calls for initial sample volume to be determined volumetrically. This SOP allows the initial sample volume to be determined by weight.

16.3.2 Section 10.2 of the method calls for the extraction to be performed with at 15% v/v methylene chloride in hexane solvent. This procedure uses methylene chloride for the extraction. SOP DV-OP-0007 calls for the methylene chloride extract to be concentrated and exchanged to hexane.

16.3.3 Section 10.2 of the method calls for shaking the separatory funnel 1-2 minutes. This SOP calls for shaking the separatory funnel for 3 minutes.

16.3.4 Section 10.2 of the method calls for allowing the organic layer to separate from the water phase for a minimum of 10 minutes. This SOP calls for allowing the organic layer to separate from the water phase for a minimum of 5 minutes after the first extraction and a minimum of 3 minutes for subsequent extractions, up to 10 minutes if the separation is not complete.

16.3.5 Section 10.3 of the method calls for rinsing the sample collection bottle with the 60 mL solvent aliquot for the second and third extraction as well as the first extraction. This SOP calls for rinsing the sample collection bottle with only the first 60-mL methylene chloride aliquot.

16.3.6 The source method does not call for the use of sodium chloride. This procedure calls for the addition of approximately 6g of sodium chloride to all samples and all QC samples in order to help the extraction efficiency.

16.4 Modifications from Method AK 102

16.4.1 Section 9.1.1.1 of the method calls for using no more than 1 liter of sample and to determine the volume either by measuring out exactly 1 liter or marking the meniscus on the sample container and later determining the volume of water required to fill the bottle back up to the mark. This SOP allows the initial sample volume to be determined by weight in order to achieve a more accurate initial volume and to avoid cross-contamination via glassware. This SOP allows for the extraction of more than 1 L as it calls for the use of the entire sample volume.

16.4.2 Section 9.1.1.6 of the method says to allow the water and solvent layers to separate for approximately 10 minutes. This SOP calls for the allowing the organic layer to separate from the water phase for a minimum of 5 minutes after the first extraction and a minimum of 3 minutes for subsequent extractions, up to 10 minutes if the separation is not complete.

16.4.3 The source method does not call for the use of sodium chloride. This procedure calls for the addition of approximately 6g of sodium chloride to all samples and all QC samples in order to help the extraction efficiency.

16.5 Modifications from Method NWTPH-Dx

16.5.1 The method calls for determining the initial volume of the sample my marking the meniscus on the bottle and later determining the volume of tap water required to fill the bottle back up to the mark. This SOP allows the initial sample volume to be determined by weight in order to achieve a more accurate initial volume and to avoid cross-contamination via glassware.

16.5.2 The method calls for shaking the separatory funnel for one minute. This SOP calls for the separatory funnel to be shaken for at least three minutes.

16.5.3 The source method does not call for the use of sodium chloride. This procedure calls for the addition of approximately 6g of sodium chloride to all samples and all QC samples in order to help the extraction efficiency.

16.6 Modifications from Oklahoma DRO

16.6.1 The method calls for aliquotting 800 mL to 900 mL of the sample volumetrically. This SOP calls for the initial sample volume to be determined by weight in order to achieve a more accurate initial volume and to avoid cross-contamination via glassware. This SOP allows for the extraction of more than 1 L as it calls for the use of the entire sample volume.

16.6.2 The method calls for extracting using 50mL of solvent. This SOP calls for the extraction to be done using at least 60mL of solvent.

16.6.3 The method calls for shaking the separatory funnel for two minutes. This SOP calls for the separatory funnel to be shaken for at least three minutes.

16.6.4 The method calls for a method blank and LCS to be analyzed every 10 samples. This SOP calls for a method blank and LCS to be analyzed every batch of 20 samples.

16.6.5 The source method does not call for the use of sodium chloride. This procedure calls for the addition of approximately 6g of sodium chloride to all samples and all QC samples in order to help the extraction efficiency.

17.0 Attachments

Table 1. Determinative Methods Using Separatory Funnel Extractions

18.0 Revision History

- **Revision 12.0, August 31, 2014**
  - Revised Section 2 to remove references to initial volume. The procedure is used on waters and leachates with a variety of initial volumes. That detail is documented later in the procedure and was therefore removed from the summary found in Section 2.
  - Added a comment to Section 9.1.2 that states: "*This procedure meets all criteria for DoD QSM 5.0 unless otherwise stated.*"
  - Section 9 was revised to remove Acceptance Criteria and Corrective Action details. This information is found in the analytical procedures.
  - Removed the Note following Section 10.4.2 that instructs the analyst to check the samples for sodium thiosulfate preservation. TestAmerica Denver does not analyze drinking water samples by this procedure and therefore this preservation is not needed.
  - All references to 8270 by LVI were removed. TestAmerica Denver does not extract samples by this procedure for 8270 by LVI. Instead the samples are extracted by 3520C under DV-OP-0008.
  - The table in Section 10.12 was revised to make it easier to read and locate the correct Method.
  - Troubleshooting and Maintenance sections were added per DoD QSM 5.0 requirements.
- **Revision 11.0, August 19, 2013**
  - Added statement to Section 2.0 that LVI must not be used on SC samples
- **Revision 10.0, May 14, 2013**
  - The procedure was revised to instruct the analyst to allow the organic and aqueous phases to separate for a minimum of 5 minutes after the first extraction and 3 minutes after subsequent extractions.
  - The procedure was revised to increase the amount of sodium chloride added to samples and QC from 3g to 6g.
  - Section 5 was revised to include the hazards of glasswool and to instruct the analysts to handle it only in a fumehood.
  - Section 8 was revised to change the hold-time calculation for leachates from the start of the leaching procedure instead of the completion of the leaching procedure. This was done to ensure the holding times are contiguous.
  - Section 10.13 was revised to instruct the analyst to extract 250mL to 100mL samples with 30mL of solvent instead of 15mL of solvent. This was done to increase extraction efficiency while still reducing solvent usage.
  - Sections 2.0, 9.1 and 10.1 were updated to reflect current practice.

- **Revision 9.0, January 15, 2013**
  - Section 10.9 was updated to include note to eliminate use of salt in South Carolina samples.
- **Revision 8.0, September 25, 2012**
  - This procedure was updated to include instructions on how to extract 8270 water samples for Large Volume Injection.
- **Revision 7.0, January 31, 2012**
  - Annual Technical Review
  - Updated Section 6.2 to describe the requirements for computer software and hardware
  - Updated Section 7.0 to describe requirements for Reagents and Standards.
  - Updated Section 8.0 to state PCBs by method 8082 have no holding time as per SW-846 Update 4 and that samples for analysis by NW-TPH have a 7 day hold time, even if acid preserved.
  - Updated Section 9.1.4 and Section 10.1 to accurately describe the NCM notification system.
  - Updated Section 10.4 and 10.6 to state the appropriate size of the graduated cylinders to be used to measure out 100mL and 200mL of leachate.
  - Updated Sections 10.6.6 and 10.14 to give guidance to the analyst when a density check of a sample is required.
  - Updated Section 10.9 to give more detail on how much sodium chloride should be added to the samples.
  - Updated Section 16 to include the method modification of the sodium chloride addition.
  - Updated Table 1 to reflect the current analytical SOPs.
  - Corrected grammatical and formatting errors

- **Revision 6.0 dated 01/10/11**
  - Added note to Section 6 that sodium sulfate should be stored in tightly closed container.
  - Revised Section 7 to reference DV-OP-00020 for information about surrogate and spike standards.
  - Corrected Section 7.1 to indicate that the reagent water should be 18 to 18.2 Mohm/cm.
  - Revised procedure to include details on the extraction of Wyoming Leachates.
  - Added references to methods NWTPH-Dx, and Oklahoma DRO.
  - Added Section 6.2 computer software and hardware.
  - Section 8 was revised to give more detail on the preservation and hold times for methods AK102, AK103, NWTPH-Dx, and Oklahoma DRO.
  - Revised Section 9 to include more detail on QC requirements for methods AK102_103, NWTPH-Dx, and Oklahoma DRO.
  - Revised Section 10 to clarify that when 1 liter graduated cylinders are used to measure the initial volume of the water samples, that the volume should be recorded to the nearest 10mL.
  - Revised Section 10 to instruct that if samples for methods AK102_103, NWTPH-Dx, and Oklahoma DRO are received preserved, then the MB and the LCS samples should also be acidified with HCl. Otherwise the samples are extracted as received.
  - Revised Section 16 to include more detail on modification from methods AK102_103, NWTPH-Dx, and Oklahoma DRO
  - Revised the procedure to call for the 2nd fraction of 8270 TCLP leachates to be extracted at a pH of 14 instead of the pH 11 to 12 used in water samples. This was done to help the recovery of pyridine.

- **Revision 5.2 dated 9/30/09**
  - Added clarification for the criteria of surrogating and spiking samples directly into the original

container.

- **Revision 5.1, dated 18 September 2009**
    - Added criteria for surrogating and spiking samples directly into the original container.
    - Added comments in Section 4 about phthalate contamination arising from gloves.
    - The procedure was revised to include the addition of approximately 3 grams of baked sodium chloride to every sample and QC sample in order to increase the ionic strength of QC samples and field QC samples to more closely match the ionic strength of typical samples and to aide in the extraction of the more polar compounds.
    - Eliminated the "short-list" 8270 LCS spike mix. All 8270 LCSs are spiked using the full list 8270/625 LCS mix, which was also revised to correct the analyte list.

- **Revision 5, dated 17 June 2009**
    - Updated Table 1 to include all determinative methods and SOPs used in conjunction with this SOP.
    - Revised Section 7.1 to define reagent water as 3 g of baked NaCl added to 1 L of water from the ELGA purification system. This was done to more closely mimic the ionic strength of environmental samples.
    - Revised Table 2 to clarify how the motor oil LCS standard is prepared and to clarify that the standards are prepared as separate working level standards.
    - Revised Table 3 to clarify that the toxaphene LCS standard is prepared as a separate standard from the organochlorine pesticide standard.
    - Revised Table 4 to add the surrogate tetrachloro-m-xylene.
    - Revised Table 5 to add compounds to the organophosphorus pesticide spike standard.
    - Revised Section 7 to delete the method 625/AFCEE standard. The laboratory uses the standard referenced in Table 7 for all method 8270 procedures, except TCLP leachates.
    - Revised the 8270 TCLP standard to correct the final concentrations.
    - Removed Attachment 1 "Organic Extractions Checklist" and added references to WI-DV-009.
    - Section 10.7 was revised to instruct the analyst to adjust the pH of samples logged in for method 8141 and 614 to a pH between 5 and 8.
    - Section 10 was revised to instruct the analyst to solvent rinse the empty sample containers for all samples, not just samples logged in for 600 series tests.

- **Revision 4, dated 13 February 2008**
    - Added information in section 5 about safety latch on the rotator.
    - Updated section 7.9 to include the expiration dates of all standards.
    - The solvent used to prepare the method 8081 spike standard described in section 7.9.5.1 has been changed to methanol to prevent the breakdown of delta-BHC. This change required the standard to have a 1 week expiration date.
    - Section 9.0 was updated to clarify the frequency requirement for LCS/LCSDs in method 608, 610,and 614.
    - Section 9.0 was revised to instruct the lab that for SW-846 method batches if a MS/MSD is not performed a LCS/LCSD is needed for precision.
    - Section 10.3 was revised to give more detail on the labs procedure for aliquoting samples gravimetrically.
    - Table 3 was revised to include alpha-chlordane.
    - Table 6 was revised to include the concentrations of both the soil and water LCS standard.
    - Table 7 was revised to add additional compounds in the spike solution.
    - Section 16 was modified to include modifications from method 614.

- **Revision 1, dated 13 February 2008**
  - Integration for TestAmerica and STL operations.

TABLE 1.

Determinative Methods Using Separatory Funnel Extractions

Method Description	*Determinative Method*	*SOP*
Diesel Range Organics & Jet Fuels	SW-846 8015, California LUFT Method, Alaska Methods AK102 & AK103 SW-846 8015C	DV-GC-0027
Chlorinated Pesticides	SW-846 8081A SW-846 8081B EPA Method 608	DV-GC-0020 DV-GC-0016
Polychlorinated Biphenyls	SW-846 8082 SW-846 8082A EPA Method 608	DV-GC-0021 DV-GC-0016
Organophosphorus Pesticides	SW-846 8141A, & EPA Method 614	DV-GC-0017
Polynuclear Aromatic Hydrocarbons (PAH)	SW-846 8310 & EPA Method 610	DV-LC-0009
Semi-volatiles by GC/MS	SW-846 8270 SW-846 8270D	DV-MS-0011 DV-MS-0012
PAH by GC/MS SIM	SW-846 8270	DV-MS-0002

Title: Analysis of Organochlorine Pesticides by High Resolution Gas Chromatography/High Resolution Mass Spectrometry

[EPA Methods 1699 and NYSDEC HRMS-2]

Approvals (Signature/Date):

5/30/14		5/30/14	
Sylvia Krenn Technical Manager	Date	Joe Schairer Health & Safety Manager / Coordinator	Date
6/17/2014		6/19/14	
Lisa Stafford Interim Quality Assurance Manager	Date	Robert Hrabak Laboratory Manager	Date

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1. SCOPE AND APPLICATION

1.1. This procedure is for the determination of the organochlorine pesticides listed in Table 1 in water, soil, sediment, sludge, tissue, sorbent resins and other sample matrices by high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS). This procedure is based on guidance from the NYSDEC Method HRMS-2 Analytical Services Protocol and additional supporting documentation found in EPA Method 1699 Pesticides in Water, Soil, Sediment, Biosolids and Tissues by HRGC/HRMS and SW846 Method 8081A.

1.2. The detection limits and quantitation levels in this procedure are usually dependent on the level of interferences rather than instrumental limitations. The minimum levels (MLs) in Table 3 are the levels at which the organochlorine pesticides can be determined with only common laboratory interferences present.

1.3. This procedure is designed for use by analysts who are experienced with residue analysis and skilled in the use of high resolution gas chromatography coupled with high resolution mass spectrometry (HRGC/HRMS).

1.4. Because of the extreme toxicity of many of these compounds, the analyst must take the necessary precautions to prevent exposure to materials known or believed to contain toxic organic compounds. It is the responsibility of the laboratory personnel to ensure that safe handling procedures are employed. Section 5 of this procedure discusses safety procedures.

2. SUMMARY OF METHOD

2.1. Extraction

2.1.1. Aqueous samples (samples containing less than one percent solids) — Stable isotopically labeled analogs of the organochlorine pesticides are spiked into a 1 L sample, and the sample is extracted using separatory funnel techniques.

2.1.2. Solid, semi-solid, and multi-phase samples (but not tissue) — The labeled compounds are spiked into a sample containing approximately 10 g of solids, and extracted for 16 hours using 1:1 methylene chloride:acetone in a Soxhlet extractor. Optionally, the samples can be extracted with toluene if requested by the client.

2.1.3. Oils, organic liquids and non-aqueous wastes — 0.1 g of the sample is diluted to 10.0 mL in methylene chloride. The dilute sample is spiked with the labeled compounds.

2.1.4. Fish and other tissue — An aliquot of sample is homogenized, and a portion is spiked with the labeled compounds. The sample is mixed with sodium sulfate, and extracted with methylene chloride in a Soxhlet extractor. An aliquot of the extract is evaporated to dryness, and the lipid content is determined.

2.2. After extraction, sample extracts may be split if required for archive. They are then cleaned up as required, and concentrated. Prior to analysis, internal standards are added to the extract.

2.3. The extract is analyzed by HRGC/HRMS. An aliquot of the sample extract is injected into the HRGC/HRMS system operating in multiple ion detection (MID) mode. The analytes are separated by the GC and detected by a high-resolution (≥ 6000 RP) mass spectrometer. Two exact m/z ratios are monitored (in most cases) for each analyte.

2.4. An individual organochlorine pesticide is identified by comparing the GC retention time and ion-abundance ratio of two exact m/z ratios with the corresponding retention time of an authentic standard and the theoretical or acquired ion-abundance ratio of the two exact m/z ratios. Chromatographic resolution for the organochlorine pesticides is achieved using capillary columns with a 5% phenyl polysiloxane standard phase. Additional analysis on a column of greater polarity may be performed if required by project objectives.

2.5. Quantitative analysis is performed using selected ion current profile (SICP) areas, using isotope dilution analyte (IDA) quantitation techniques, based on whether a labeled analog is available for a given analyte.

3. DEFINITIONS

3.1. Estimated Detection Limit (EDL): The sample specific estimated detection limit (EDL) is the concentration of a given analyte required to produce a signal with a peak height of at least 2.5 times the background signal level.

3.2. Estimated Maximum Possible Concentration (EMPC): The calculated concentration of a signal having the same retention time as a target pesticide but which does not meet the other qualitative identification criteria defined in the procedure.

3.3. Minimum Level (ML): The level at which the entire analytical system must give a recognizable signal and acceptable calibration. It is equivalent to the concentration of the lowest calibration standard, assuming that all method-specified sample weights, volumes, and cleanup procedures have been employed.

3.4. Definitions of other terms used in this SOP may be found in the glossary of the Laboratory Quality Assurance Manual (QAM).

3.5. Data qualifiers are defined on each data report. Commonly used data qualifiers are defined in the QAM.

4. INTERFERENCES

4.1. Solvents, reagents, glassware and other sample processing hardware may yield discrete artifacts or elevated baselines that may cause misinterpretation of the chromatographic data. All of these materials must be demonstrated to be free from interferences under the conditions of analysis by performing laboratory method blanks. Analysts should avoid using PVC gloves, powdered gloves, or gloves with measurable levels of phthalates.

4.2. The use of high purity reagents and solvents helps minimize interference problems. Purification of solvents by distillation in all-glass systems may be necessary.

4.3. Interferences co-extracted from the samples will vary considerably from matrix to matrix. Pesticides are often associated with other interfering chlorinated substances such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDDs and PCDFs), polychlorinated diphenyl ethers (PCDPEs), polychlorinated naphthalenes, polychlorinated alkyldibenzofurans, methoxy biphenyls, hydroxy-diphenyl ethers, benzylphenyl ethers, polynuclear aromatics, and polychlorinated biphenyls. Because very low levels of organochlorine pesticides are measured by this method, the elimination of interferences is essential. The cleanup steps given in Section 11.5 can be used to reduce or eliminate these interferences and thereby permit reliable determination of the organochlorine pesticides at the levels shown in Table 3.

4.3.1. Screening procedures or other analytical procedures have been shown to help identify correct sample sizes to help mitigate high analyte content or high matrix background.

4.3.1.1. Pesticide screening by GC/ECD may be used to identify samples that have high target analytes. Using this simple screening technique along with a sulfur removal step will allow a corrected sample size to be used to not saturate the High Resolution detector for any single target pesticide analyte.

4.3.1.2. PAH screening by GC/FID or using results from a PAH analysis (Method 8270C) may be used to identify samples that have gross levels of total PAH loading. It has been shown that samples containing greater than 10ug/g of total PAH will negatively affect the DDE/DDD/DDT traces. In the event a total PAH concentration is found in a sample, a reduced sample size should be used (start with 1/10 the normal extraction).

4.4. Glassware cleaning is performed in accordance with SOP WS-OP-0011.

4.4.1. Immediately prior to use, the Soxhlet apparatus should be pre-extracted with methylene chloride or toluene, dependent upon the analyses requested, for a minimum of 4 hours.

4.4.2. Alternately glassware may washed with soap and water followed by kilning the glassware at 400°C for at least 2 hours.

4.5. All materials used in the analysis shall be demonstrated to be free from interferences by running reference matrix method blanks (Section 9.6) initially and with each sample batch.

4.6. The natural lipid content of tissue can interfere in the analysis of tissue samples for the organochlorine pesticides. The lipid contents of different species and portions of tissue can vary widely. Lipids are soluble to varying degrees in various organic solvents and may be present in sufficient quantity to overwhelm the column chromatographic cleanup procedures used for cleanup of sample extracts. Additional cleanup procedures may be performed if necessary.

5. SAFETY

Employees must abide by the policies and procedures in the Corporate Environmental Health and Safety Manual (CW-E-M-001), the Sacramento Addendum to the Corporate EH&S Manual (WS-PEHS-002) and this document. This procedure may involve hazardous material, operations and equipment. This SOP does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of the method to follow appropriate safety, waste disposal and health practices under the assumption that all samples and reagents are potentially hazardous. Safety glasses, gloves, lab coats and closed-toes, nonabsorbent shoes are a minimum.

5.1. Specific Safety Concerns or Requirements

5.1.1. Eye protection that satisfies ANSI Z87.1, laboratory coat, and chemically resistant gloves must be worn while samples, standards, solvents, and reagents are being handled. Nitrile gloves should be used when performing this extraction. Latex and vinyl gloves provide no significant protection against the organic solvents used in this SOP, and should not be used.

5.1.2. Exposure to chemicals must be maintained **as low as reasonably achievable**, therefore all samples must be opened, transferred and prepared in a fume hood. Solvent and waste containers will be kept closed unless transfers are being made.

5.1.3. Laboratory procedures such as repetitive use of pipets, repetitive transferring of extracts, and manipulation of filled separatory funnels and other glassware represent a significant potential for repetitive motion or other ergonomic injuries. Laboratory associates performing these procedures are in the best position to realize when they are at risk for these types of injuries. Whenever a situation is found in which an employee is performing the same repetitive motion, the employee shall immediately bring this to the attention of their supervisor, manager, or the EH&S staff. The task will be analyzed to determine a better means of accomplishing it.

5.1.4. Mercury is a highly toxic compound that must be handled with care. The analyst must be aware of the handling and clean-up techniques before handling this material. The Emergency Response Team must be activated for any mercury spills.

5.1.5. Assembly and disassembly of glassware creates a risk of breakage and cuts. All staff members shall wear Kevlar® or similar cut-resistant gloves over chemically resistant gloves when assembling and disassembling glassware.

5.1.6. The use of vacuum systems during Florisil cartridge cleanup presents the risk of imploding glassware. All glassware used during vacuum operations must be thoroughly inspected prior to each use. Glass that is chipped, scratched, cracked, rubbed or marred in any manner must not be used under vacuum. It must be removed from service and replaced.

5.1.7. Exercise caution when using syringes with attached filter assemblies. Application of excessive force has, on occasion, caused a filter disc to burst during the process.

5.1.8. Ensure that the vacuum exhaust hose used during the Florisil cartridge cleanup is securely anchored inside of a fume hood so that solvent vapors are not pumped into the working environment.

5.1.9. The use of separatory funnels to extract aqueous samples with methylene chloride creates excessive pressure very rapidly. Initial venting should be done immediately after the sample container has been sealed and inverted. Vent the funnel into the hood away from people and other samples. This is considered a high-risk activity, and a face shield must be worn over safety glasses or goggles when it is performed.

5.1.10. The effluents of sample splitters for the gas chromatograph and roughing pumps on the HRGC/HRMS system should pass through either a column of activated charcoal or be bubbled through a trap containing oil or high-boiling alcohols.

5.1.11. Hearing protection must be worn when using mechanical systems to grind fish or tissue samples.

5.1.12. When Dean-Stark/Soxhlet/CLLE clean-ups or extractions are performed overnight or unattended, special precautions must be taken. Open the chiller valves to the system about 15 minutes before the heating elements are turned on, and check every condenser to ensure that it is cold and functioning properly. Check every condenser again about 15 minutes after turning on the heating elements to ensure they are still cold and functioning properly. If the system is left operating overnight or unattended for an extended period, the first chemist to come back into the lab must again check every condenser to ensure that it is still cold and functioning properly.

5.1.13. If sediment/soil samples have been frozen in glass jars, the freezing process may cracked the jars when the sample expanded during freezing. After the samples have thawed, wear cut protective gloves while handling the jars until it can be confirmed that the jars have not cracked.

5.2. PRIMARY MATERIALS USED

The following is a list of the materials used in this method, which have a serious or significant hazard rating. NOTE: This list does not include all materials used in the method. The table contains a summary of the primary hazards listed in the SDS for each of the materials listed in the table. A complete list of materials used in the method can be found in the reagents and materials section. Employees must review the information in the SDS for each material before using it for the first time or when there are major changes to the SDS.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Acetone	Flammable	1000 ppm-TWA	Inhalation of vapors irritates the respiratory tract. May cause coughing, dizziness, dullness, and headache.
Dodecane	Flammable	None listed	May cause respiratory tract, skin or eye irritation.
Hexane	Flammable Irritant	500 ppm-TWA	Inhalation of vapors irritates the respiratory tract. Overexposure may cause lightheadedness, nausea, headache, and blurred vision. Vapors may cause irritation to the skin and eyes.

Material (1)	Hazards	Exposure Limit (2)	Signs and symptoms of exposure
Isooctane	Flammable	500 ppm TWA	Causes eye or respiratory tract irritation. Repeated prolonged exposure can cause defatting of skin. High concentrations can produce drowsiness.
Mercury	Poison	0.1 mg/M3 Ceiling (Mercury Compounds)	Extremely toxic. Causes irritation to the respiratory tract. Causes irritation. Symptoms include redness and pain. May cause burns. May cause sensitization. Can be absorbed through the skin with symptoms to parallel ingestion. **May affect the central nervous system.** Causes irritation and burns to eyes. Symptoms include redness, pain, and blurred vision; may cause serious and permanent eye damage.
Methylene Chloride	Carcinogen Irritant	25 ppm-TWA 125 ppm-STEL	Causes irritation to respiratory tract. Has a strong narcotic effect with symptoms of mental confusion, light-headedness, fatigue, nausea, vomiting and headache. Causes irritation, redness and pain to the skin and eyes. Prolonged contact can cause burns. Liquid degreases the skin. May be absorbed through skin.
Nonane	Flammable	200 ppm	Primary hazard is flammability. May also cause skin irritation, drowsiness, and dizziness if inhaled.
Toluene	Flammable Poison Irritant	200 ppm-TWA 300 ppm-Ceiling	Inhalation may cause irritation of the upper respiratory tract. Symptoms of overexposure may include fatigue, confusion, headache, dizziness and drowsiness. Peculiar skin sensations (e. g. pins and needles) or numbness may be produced. Causes severe eye and skin irritation with redness and pain. May be absorbed through the skin.
1 – Always add acid to water to prevent violent reactions.			
2 – Exposure limit refers to the OSHA regulatory exposure limit.			

6. EQUIPMENT AND SUPPLIES

6.1. Equipment for sample preparation.

Note: All glassware used in extraction and cleanup procedures is solvent rinsed before use with acetone, toluene, hexane and methylene chloride in that order. Pre-extract Soxhlet apparatus with methylene chloride or toluene, dependent upon analyses requested, for at least 4 hours.

6.1.1. Laboratory fume hood of sufficient size to contain the sample preparation equipment listed below.

6.1.2. Blender with glass cup and aluminum foil for lid.

6.1.3. Hobart brand food grinder or equivalent.

6.1.4. Analytical balance, capable of weighing to 0.01 g.

6.1.5. Oven - Capable of maintaining a temperature of 110 ± 5°C

6.1.6. 2000 mL separatory funnels with PTFE stopcocks and glass stoppers.

6.1.7. 100 mm glass funnel with short stem.

6.1.8. 500 mL round bottom flask.

6.1.9. Class A 1 mL pipettes.

6.1.10. 250 and 1000 mL graduated cylinders.

6.1.11. Glass wool.

6.1.12. Nitrogen evaporator (standard).

6.1.13. "Turbo-Vap" nitrogen evaporator.

6.1.14. Borosilicate 5.75" and 9" disposable pipettes.

6.1.15. Borosilicate 40 mL disposable vials.

6.1.16. Soxhlet apparatus, consisting of Dean-Stark extraction apparatus, heating mantles with temperature controls, 500 mL round bottom flask, and glass condenser, capable of sitting on top of the Soxhlet extractor.

6.1.17. PTFE boiling chips (methylene chloride rinsed).

6.1.18. 40 mL vial, with PTFE-lined cap.

6.1.19. Rotary evaporator (Buchi or equivalent).

6.1.20. Whatman high purity glass fiber thimbles.

6.1.21. Syringe filter, 0.45 um.

6.1.22. Florisil cartridges — 6 ml glass cartridges with a PTFE frit and packed with 1 g Florisil. All HRMS disposable columns are stored in the oven at 120ºC and solvent rinsed with hexane before use.

6.1.23. Mini vials, 1.1 mL capacity with a tapered bottom; with PTFE-faced, rubber septa and screw caps.

6.1.24. 20 mm ID column for custom Florisil column or custom Silica Gel column cleanups.

6.2. Gel Permeation Chromatograph (GPC) — J2 Scientific Accuprep MPS or equivalent. Equipped with biobead S-X3 resin or equivalent. See WS-OP-0012 for GPC specific information.

6.3. Gas Chromatograph (GC) — Equipped with splitless or on-column injection port for capillary column, temperature program with isothermal hold, and capable of meeting all of the performance specifications in Section 11.

6.3.1. GC Column: 60 m x 0.32 mm ID x 0.25 um film thickness DB-5 or RTX-5 fused silica capillary column (J&W No. 123-5062 or Restek No.10227) or equivalent.

6.4. Mass Spectrometer (MS) — Electron impact ionization with the filament electron energy between 30eV-40eV and optimized for best instrument sensitivity, stability and signal-to-noise ratio. Shall be capable of repetitively and selectively monitoring a minimum of 14 exact m/z at high resolution (≥6000) during a period of approximately 1 second and shall meet all of the performance specifications in Section 11.

6.5. This laboratory operates an Agilent GC 7890A/6890N and Autospec Premier mass spec which utilizes Masslynx v4.1 and Chrom Peak Review, version 2.1 software or equivalent.

6.6. GC/MS Interface — The mass spectrometer (MS) shall be interfaced to the GC such that the end of the capillary column terminates within 1 cm of the ion source but does not intercept the electron or ion beam.

6.7. Data System — Capable of collecting, recording, and storing MS data.

7. REAGENTS AND STANDARDS

7.1. Reagent water.

7.2. Acetone, pesticide quality and glass distilled, or equivalent.

7.3. Hexane, pesticide quality and glass distilled, or equivalent.

7.4. Methylene chloride, pesticide quality and glass distilled, or equivalent.

7.5. Toluene, 99.9%.

7.6. Dodecane, high purity, distilled in glass or highest available purity.

7.7. Isooctane (2,2,4-Trimethyl Pentane), high purity, distilled in glass or highest available purity.

7.8. Sodium sulfate, ACS, anhydrous, granular, rinsed with methylene chloride. Store in a 4 L AGB until use.

7.9. Silica gel (60/100 mesh). Pre-rinse with methylene chloride and oven dried. Store in an oven at 110°C to 130°C.

7.10. Silica gel (60/100 mesh).

7.11. Florisil, Pesticide residue (PR) grade (60/100) mesh; purchased pre-packed (1 g) in glass cartridges with PTFE frits. See Section 11.5.6.

7.12. Perfluorokerosene (PFK) high boiling mass spectroscopy grade; bp 210-260°C; d^{20}_{4} 1.94; n^{20}_{D} 1.330; Fluka (Catalog No. - 77275).

7.13. Mercury, triple distilled.

7.14. GPC calibration solution (see WS-OP-0012).

7.15. Spiking Standards and Calibration Solutions:

7.15.1. Prior to using purchased standard materials, verify that the purity of each component is ≥ 97%.

7.15.1.1. For neat materials, if the purity of a neat material is ≥ 97%, no further action is required. If the purity is < 97%, correct the concentration of any solution prepared from the neat for the purity, i.e., a solution of 100 ug/mL would contain 97 ug/mL of the compound of interest.

7.15.1.2. For solutions, if the purity of each compound is ≥ 97%, no further action is required. If the purity for a compound is < 97%, verify that the vendors have accommodated this value in their calculations. If not, the laboratory should correct the concentrations based on the purity prior to using the solution.

7.15.2. Native organochlorine pesticide standard solutions are Certified Reference Standards such as available from Radian International Analytical Reference Materials Inc. (Austin TX). Catalog numbers 1647B, 1648B and 1649B (or equivalent). Stock solutions are purchased at 100 ug/mL in hexane (with up to 5% toluene). The native standards are received in 3 mixes and are combined and diluted to produce the intermediate stocks (see Section 7.15.3.1). Expiration dates of native stocks and standards are 6 months, or manufacturer's expiration date, which ever is sooner. Standards are re-verified after 6 months according to WS-QA-0017.

7.15.2.1. Toxaphene is a separate solution and can be purchased as a Certified Reference Standard from Ultra Scientific or other certified vendors. Catalog number PP-271 (or equivalent). Stock solutions are purchased at 100 ug/mL in hexane.

7.15.3. Labeled pesticide solutions used are Certified Reference Standards purchased from Cambridge Isotope Laboratories (CIL, Andover Massachusetts). Most stock solutions are purchased at 100 ug/mL in nonane. The contents of the ampoules are transferred to amber glass vials with fluoropolymer-lined caps after being brought to room temperature and are used as received. Some variability in the certified concentration has been noted, with lot specific certificates of analysis ranging from 89 to 100 ug/mL. The volumes of standards used are adjusted to normalize amounts in the working stocks. Expiration dates of labeled pesticide stocks and standards are 10 years, or manufacturer's expiration date, which ever is sooner. The labeled standards are used for relative quantitation. Instruments are recalibrated annually to account for any changes in isotope dilution analyte concentration.

7.15.3.1. Intermediate native target stock solution: Prepared by combining each of the three (3) individual stock solutions of the native pesticides listed in Section 7.15.2 and diluting to a final concentration of 20 ng/mL in isooctane.

7.15.3.2. Toxaphene native solution: Prepared by diluting the solution listed in Section 7.9.1.1 to a final concentration of 10,000 ng/mL in isooctane.

7.15.3.3. Labeled isotope dilution analyte stock solution: Prepared by combining the individual stock solutions of the labeled isotope dilution analytes (Table 4) and diluting to a final concentration of 20 ng/mL in isooctane.

7.15.3.4. Labeled internal standard stock solution: Prepared by diluting the individual stock solutions of the labeled internalstandards (Table 4) to a concentration of 100 ng/mL in dodecane.

7.15.4. Calibration solutions are prepared by dilution of the mixed stock standard solutions prepared above in nonane. Table 4 shows the calibration solutions components and final concentrations.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1. Grab and composite samples must be collected in glass containers. Conventional sampling practices must be followed. The bottle must not be prewashed with sample before collection. Composite samples should be collected in glass containers. Sampling equipment must be free of Tygon, rubber tubing, or other potential sources of contamination that may absorb the target analytes.

8.2. Store aqueous samples in the dark at 4 ± 2°C. Samples must be extracted within 7 days of collection to meet holding time criteria.

8.3. Store solid, semi-solid, oily, and mixed-phase samples in the dark at less than -10°C. Samples must be extracted within 1 year of collection to meet holding time criteria.

8.4. Fish and tissue samples

8.4.1. Fish may be cleaned, filleted, or processed in other ways in the field, such that the laboratory may expect to receive whole fish, fish fillets, or other tissues for analysis.

8.4.2. Fish collected in the field should be wrapped in aluminum foil, and must be maintained at a temperature less than 6°C from the time of collection until receipt at the laboratory.

8.4.3. Samples must be frozen upon receipt at the laboratory and maintained in the dark at less than -10°C until prepared. Prepare samples within one year of collection to meet holding time criteria. Maintain unused sample in the dark at less than -10°C.

8.5. Store sample extracts in the dark in glass vials at room temperature until analyzed. Analyze samples within 40 days of extraction to meet holding time criteria.

8.5.1. If stored in the dark at less than -10°C, sample extracts may be stored for up to one year to meet holding time criteria.

9. QUALITY CONTROL

9.1. Initial Demonstration of Capability

The initial demonstration and method detection limit (MDL) studies described in Section 13 must be acceptable before analysis of samples may begin.

9.2. Quality Control Batch

The batch is a set of up to 20 field samples that are of the same matrix and are processed together using the same procedures and reagents. The batch must contain a method blank and an LCS (OPR).

Batches are defined at the sample preparation stage. Batches should be kept together through the whole analytical process as far as possible, but it is not mandatory to analyze prepared extracts on the same instrument or in the same sequence. Refer to the QC Program document (WS-PQA-003) for further details of the batch definition.

9.3. Control Limits

In-house historical control limits must be determined for ongoing precision and recovery samples (OPR). These limits must be determined at least annually. The recovery limits are mean recovery ±3 standard deviations.

9.3.1. Default limits are listed in Table 7. These limits are used to evaluate both OPR and Matrix Spike/Matrix Spike Duplicates (MS/MSD) samples. In-house control limits should be determined when sufficient data are available.

9.3.2. All isotope dilution analytes and OPR recoveries must be entered into QuantIMS or other database so that accurate historical control limits can be generated.

9.3.3. Refer to the Policy WS-PQA-003 for further details of control limits.

9.4. Labeled Isotope Dilution Analytes

Every sample, blank, and QC sample is spiked with isotope dilution analytes. Isotope dilution analyte recoveries in samples, blanks, and QC samples must be assessed to ensure that recoveries are within established limits and determine the effect of matrix on the method performance. The compounds included in the isotope dilution analyte spiking solutions are listed in Table 4. When properly applied, results from isotope dilution techniques are independent of recovery. The recovery of each isotope dilution analyte should be within the limits listed in Table 7. If the recovery is outside these limits the following corrective action should be taken:

- Check all calculations for error.
- Ensure that instrument performance is acceptable.
- Recalculate the data and/or reanalyze if either of the above checks reveal a problem.
- If the recovery of any isotope dilution analyteis less than 20 percent, calculate the S/N ratio of the isotope dilution analyte. If the S/N is > 10 and the estimated detection limits (EDLs) are less than the minimum levels (MLs), report the data "as is" with qualifiers in the report and a discussion in the case narrative. If the S/N is < 10 or the estimated detection limits (EDLs) are greater than the minimum levels (MLs), re-extract and re-analyze the sample if sufficient sample is available, otherwise qualify data and narrate. If the poor isotope dilution analyte recovery is judged to be a result of sample matrix, a reduced portion of the sample may be re-extracted or additional clean-ups may be employed. The decision to reanalyze or flag the data should be made in consultation with the client.

9.4.1. Refer to WS-PQA-003 for further details of the corrective actions.

9.4.2. Recovery of isotope dilution analytes from samples must be entered into the TALS database for determining control limit adjustments.

9.5. GC Resolution and monitoring of compound breakdown

9.5.1. For both initial and continuing calibrations, evaluate the chromatographic separation between 4,4'-DDD and 2,4'-DDT. While monitoring mass 235.008, the valley between 4,4'-DDD and 2,4'-DDT must have a valley height of less than 20% when compared to the height of the smaller peak.

9.5.2. DDT breakdown

9.5.2.1. Evaluate the DDT breakdown in the continuing calibration verification (CCV) at the beginning of each shift. The %Deviation of $^{13}C_{12}$-2,4'-DDT is compared to the %D for $^{13}C_{12}$-2,4'-DDD; and the %D for $^{13}C_{12}$-4,4'-DDT is compared to the %D of $^{13}C_{12}$-4,4'-DDD. If the %D of the $^{13}C_{12}$-DDT isomers are negative from the calibration and the %D of the $^{13}C_{12}$-DDD isomers are positive, DDT breakdown is suspected. If the %D for a $^{13}C_{12}$-DDT falls below the lower acceptance criterion, or the %D for a $^{13}C_{12}$-DDD is above the upper acceptance criterion, GC maintenance is performed. To facilitate consistency, the acceptance criteria for % D for these analytes have been tightened to 50% to 150% in the CCV (Table 8).

9.5.2.2. DDT breakdown may occur in field samples and can be identified when $^{13}C_{12}$-2,4'-DDT or $^{13}C_{12}$-4,4'-DDT percent recovery falls below 40%.

9.5.2.2.1. If the percent recovery of $^{13}C_{12}$-2,4'-DDT or $^{13}C_{12}$-4,4'-DDT falls below 40% but subsequent sample or QC injections are within control then DDT breakdown is less of an impact and the isotope dilution calculation will normalize to the lower than normal isotope dilution analyte recovery.

9.5.2.2.2. If the percent recovery of $^{13}C_{12}$-2,4'-DDT or $^{13}C_{12}$-4,4'-DDT falls below 20% and subsequent sample or QC injections continues to decrease then DDT breakdown is likely to have occured. Replace the liner, retune the instrument, re-inject the affected samples (preferrably in a different injection order) and confirm the low recovery. If the recoveries are similar, then DDT breakdown is less of an impact and the isotope dilution calculation will normalize to the lower than normal isotope dilution analyte recovery.

9.5.2.2.3. If $^{13}C_{12}$-2,4'-DDT and/or $^{13}C_{12}$-4,4'-DDT are not present, then re-analyze the extract (preferrably in a different injection order). If the re-injection shows recoveries then evaluate recoveries as stated in Section 9.5.2.2. If the isotope dilution analytes are still not present after re-analyzing the samples, then either take a smaller aliquot from the archive and re-clean/re-analyze or re-extract a smaller sample size.

9.5.3. Endrin breakdown has not been shown to happen on the Mass Spectrometer system. Endrin is susceptible to have losses in either the concentration step or having acetone present in the extract prior to processing the sample through the silica gel column.

9.5.4. Each OC pesticide is resolved from others by a 40% valley, measured from the smaller peak of the pair. Note: each target analyte referenced in this method is either in a mass by itself or has baseline chromatography resolution from the next closest analyte if using the analytical experiment used in this method.

9.5.4.1. If this requirement is not achieved and the sample has a positive concentration for the compound of interest, perform column maintenance. If that does not resolve the issue, the following may be conducted:

9.5.4.1.1. The extract can be fractionated to isolate each compound in a separate fraction.

9.5.4.1.2. Additional GC columns that meet this requirement may be used that resolve the compounds of interest.

9.6. Method Blanks

A laboratory method blank must be run along with each analytical batch of 20 or fewer samples. The method blank is normally analyzed immediately after the calibration standards. An instrument blank is recommended to run before the method blank to evaluate method blank contamination. An instrument blank consists of reagent blank dodecane solvent. The method blank consists of reagent water for aqueous samples, and a clean solid matrix (sand, sodium sulfate, etc.) for solid samples. The method blank must not contain any analyte of interest at or above the minimum levels (ML) or at or above 10% of the measured concentration of that analyte in the associated samples, whichever is higher.

- Reanalysis of samples associated with an unacceptable method blank is required when reportable concentrations are determined in the samples unless the sample results exceed 10X the blank value.
- If there is no target analyte greater than the minimum levels (ML) in the samples associated with an unacceptable method blank, the data may be reported with qualifiers. Such action should be done in consultation with the client.

9.6.1. The method blank must have acceptable isotope dilution analyte recoveries. If recoveries are not acceptable, the data must be evaluated to determine if the method blank has served the purpose of demonstrating that the analysis is free of contamination (i.e. evaluate the estimated detection limit by using the noise). If isotope dilution analyte recoveries are low and there are reportable analytes in the associated samples re-extraction of the blank and affected samples will normally be required. Consultation with the client should take place.

9.6.2. If reanalysis of the batch is not possible due to limited sample volume or other constraints, the method blank is reported, all associated samples are flagged with a "B," and appropriate comments may be made in a narrative to provide further documentation.

9.6.3. Refer to WS-PQA-003 for further details of the corrective actions.

9.7. Instrument Blank

Instruments must be evaluated for contamination after calibration and before client sample analysis during each 12 hour analytical run. This may be accomplished by analysis of a method blank. If a method blank is not available, an instrument blank must be analyzed. An instrument blank consists of reagent grade dodecane solvent.

9.7.1. Instrument rinse solvents. Rinse instrument needle with isooctane followed by dodecane. Rinsing the needle in this order will greatly reduce sample carry over due to the injection needle.

9.8. Laboratory Control Samples (LCS or OPR)

9.8.1. For each batch of samples, analyze an OPR. The OPR contains a representative subset of the analytes of interest, and must contain the same analytes as the matrix spike. The OPR may also contain the full set of analytes. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur.

9.8.1.1. If toxaphene is requested, then a second OPR is spiked with the pesticide isotope dilution analyte and toxaphene native standard.

9.8.2. OPR compound lists are included in Table 7.

9.8.3. The standard OPR spike mix does not include Toxaphene. These spikes are in addition to and will require separate OPR aliquots.

9.8.4. If any analyte in the OPR is outside the laboratory established historical control limits, corrective action must occur:

- Check calculations,
- Check instrument performance,
- Evaluate the data, and/or
- Reanalyze the OPR, and if still outside of control limits,
- Re-prepare and reanalyze all samples in the QC batch.

9.8.5. Data may be reported with an anomaly in the following cases:

- The OPR recoveries are high and the analyte of concern is not detected in field samples, or
- All target requested analytes are within control, but other OPR compounds are out of control.

9.8.6. The analyst should evaluate the anomalous analyte recovery for possible trends.

9.8.7. If the batch is not re-extracted and reanalyzed, the reasons for accepting the batch must be clearly presented in the project records and the report.

9.8.8. If re-extraction and reanalysis of the batch is not possible due to limited sample volume or other constraints, the OPR is reported, all associated samples are flagged, and appropriate comments are made in a narrative to provide further documentation.

9.8.9. Refer to WS-PQA-003 for further details of the corrective action.

9.9. Matrix Spikes/Matrix Spike Duplicates

9.9.1 Matrix Spike/Matrix Spike Duplicates (MS/MSD) are performed on a client request basis only. The MS/MSD contains a representative subset of the analytes of interest, and must contain the same analytes as the OPR. The MS/MSD may also contain the full set of analytes. If any analyte or surrogate is outside established control limits, the system is out of control and corrective action must occur.

9.9.1.1 If toxaphene is requested, then a second MS/MSD is spiked with the pesticide isotope dilution analyte and toxaphene native standard

9.9.2 MS/MSD compound lists are included in Table 7.

9.9.3 The standard matrix spike mix does not include toxaphene. These spikes are in addition to and will require separate MS/MSD aliquots.

9.9.4 If any analyte in the MS/MSD is outside the laboratory established historical control limits, corrective action must occur:

- Check calculations,
- Check instrument performance,
- Evaluate the data

9.9.5 Data may be reported with an anomaly in the following case:

- The associated OPR recoveries are in control, thus indicating the anomalous MS/MSD recoveries to be matrix related.

9.10. Nonconformance and Corrective Action

Any deviations from QC procedures must be documented as a nonconformance, with applicable cause and corrective action approved by the QA Manager.

9.11. Quality Assurance Summaries

Certain clients may require specific project or program QC which may supersede these method requirements. Quality Assurance Summaries should be developed to address these requirements.

9.12. QC Program

Further details of QC and corrective action guidelines are presented in the QC Program document (WS-PQA-003). Refer to this document if in doubt regarding corrective actions.

10. CALIBRATION

10.1. On a daily basis, calibrate any balances to be used in accordance with SOP WS-QA-0041.

10.2. With the exception of instances detailed in Policy CA-P-T-002, it is NOT acceptable to remove points from a calibration curve for the purpose of meeting criteria, unless the points are the highest or lowest on the curve AND the reporting limit and/or linear range is adjusted accordingly. In any event, at least 5 points must be included in the calibration curve. Quadratic (second order) calibrations require at least six points.

10.3. Initial Calibration

Prior to sample analysis, a multi-point initial calibration must be analyzed and evaluated. This calibration is repeated when a continuing calibration fails the criteria in Section 10.5.

10.3.1. Prepare multi-level calibration standards containing the compounds and concentrations as specified in Table 4. Store in the dark. Use Table 4A for the multi-level calibration of toxaphene.

10.3.2. Establish operating parameters for the GC/MS system. By using a PFK molecular leak, tune the instrument (see the appropriate instrument manufacturer's operating manual for tuning instructions) to meet the minimum resolving power of 6000 (10 percent valley) across all monitored functions and a resolving power of at least 8000 at a mass in the monitored function.

10.3.2.1. Toxaphene analysis is required to meet 1000 minimum resolving power (10 percent valley) at m/z 168.9888.

10.3.3. Analyze 1 to 2 µL of the CS1 calibration standard. Verify that the signal-to-noise ratio of the extracted ion profile for endosulfan I is $\geq$ 2.5.

10.3.4. Set the descriptor switch points to times midway between the windowing compounds.

10.3.5. Analyze 1 to 2 µL of at least five calibration standards and calculate the RRF of each analyte vs. the appropriate isotope dilution analyte using the following equation:

Equation 1

$$RRF = \frac{A_s \times C_{IDA}}{A_{IDA} \times C_S}$$

Where:

A_s = sum of the areas of the quantitation ions of the compound of interest

A_{IDA} = sum of the areas of the quantitation ions of the appropriate standard

C_{IDA} = concentration of the appropriate standard

C_s = concentration of the compound of interest

10.3.5.1. Toxaphene RRFs are generated for each of the five characteristic markers, using the concentration of the standard solution as the concentration of the marker. At least 3 of the 5 markers must be used to qualitatively identify toxaphene.

10.3.6. Calculate the mean RRF and the RSD of the relative response factors for each target analyte. The RSD for the mean RRFs for each unlabelled target analyte with a matching labeled isotope dilution analyte should not exceed 20%.

10.3.6.1. A mean RRF and RSD for toxaphene is calculated for each of the five characteristic markers. An average RSD for all toxaphene is calculated from the RSD from the individual characteristic markers. The average RSD for the mean RRF for toxaphene should not exceed 35%.

10.3.7. Calculate the mean RRF and the RSD of the relative response factors for each labeled isotope dilution analyte. The RSD for the mean RRFs for each labeled target analyte against its surrogate should not exceed 35%.

10.3.8. Verify that the S/N for the GC signals present in every SICP is ≥ 10 for labeled standards, SICP ≥ 2.5 for natives.

10.3.9. Verify that the ion abundance ratios are within the control limits specified in Table 6.

10.3.10. If the criteria in Sections 10.3.6 – 10.3.9 are not met, identify the root cause, perform corrective action, and repeat the initial calibration. If the root cause can be traced to problems with an individual analysis within the calibration series, repeat the individual analysis and recalculate the percent relative standard deviation. If the calibration is acceptable, document the problem and proceed otherwise repeat the initial calibration. Daily calibration checks will be used to verify that the calibration is still valid until the continuing calibration criteria in Section 10.5.2 are no longer met. At such time, a new initial calibration will be performed.

10.4. Initial Calibration Verification (ICV) — When available, a second source standard is analyzed with the initial calibration curve. Each compound of the ICV must be within ± 30% of its expected value. Corrective actions for the ICV include:

- Rerun the ICV
- Remake or acquire a new ICV
- Evaluate the instrument conditions
- Evaluate the Initial Calibration Standards

10.4.1. Toxaphene concentration is calculated by first calculating the concentration of each of the 3 to 5 markers, using the RRF for each marker. Then concentrations of the 3 to 5 markers are averaged to calculate the concentration of toxaphene in the ICV.

10.5. Continuing Calibration Verification (CCV) — A CCV is performed at the beginning of a 12-hour period and must meet the criteria below. If the laboratory is operating consecutive 12 hour shifts a CCV must be performed at the beginning of every 12 hour shift.

10.5.1. Before analyzing the CCV, perform the mass resolution check detailed in Section 10.3.2. If the check passes criteria, a continuing calibration may be analyzed. Otherwise, corrective action such as instrument maintenance and re-tuning may be required.

10.5.2. Analyze 1 to 2 μL of the CS4 or CS5 Verification standard solution under the same instrument conditions used to perform the initial calibration. Confirm that the first and last eluters listed in Table 5 elute within the proper MID descriptor window. Adjust the switch points if necessary.

10.5.2.1. Calculate the daily RRFs using Equation 1. The percent drift (%D) between the measured RRFs and the mean values established during the initial calibration (Section 10.3.6) for the unlabeled native analytes must be within the acceptance limits in Table 8.

10.5.2.1.1. Toxaphene concentration is calculated by first calculating the concentration of each of the 3 to 5 markers, using the RRF for each marker. Then concentrations of the 3 to 5 markers are averaged to calculate the concentration of toxaphene in the CCV. The percent difference (%D) of the CCV is evaluated to be within the acceptance limits in Table 8.

10.5.2.2. The measured RRFs for the labeled isotope dilution analytes should be within the acceptance limits in Table 8. Values exceeding these limits may be used if the corresponding native RRFs are within the limits specified above. In this case, the return to control must be demonstrated for the labeled isotope dilution analytes prior to additional sample analysis.

10.5.2.3. The chromatographic resolution criteria specified in Section 9.5 must be met for the specified analytes.

10.5.2.4. The ion abundance ratios must be within the control limits specified Table 6.

10.5.2.5. Removed section.

10.5.2.6. The retention time for methoxychlor must be greater than 31 minutes.

10.5.2.7. If the criteria above are not met, identify the root cause, perform corrective action, and repeat the continuing calibration. Continued failure of the continuing calibration may indicate the need for further maintenance and a new initial calibration.

11. PROCEDURE

11.1. One time procedural variations are allowed only if deemed necessary in the professional judgment of a supervisor to accommodate variation in sample matrix, radioactivity, chemistry, sample size, or other parameters. Any variation in procedure shall be completely documented using a Nonconformance Memo and is approved by a Technical Specialist and QA Manager. If contractually required, the client shall be notified. The Nonconformance Memo shall be filed in the project file.

11.2. Any unauthorized deviations from this procedure must also be documented as a nonconformance, with a cause and corrective action described.

11.3. Sample Extraction

Samples are extracted by the following procedures depending upon sample matrix. Water samples are prepared by separatory funnel. Solid samples including soils, sediments, tissues, XAD tubes, PUF cartridges, and solid waste materials are prepared by Soxhlet extraction. Non-aqueous liquid wastes and organic solvents are prepared by waste dilution techniques.

NOTE: Samples should be removed from the refrigerator or freezer several hours before extraction and allowed to come to room temperature before measuring the volume or performing the extraction.

11.3.1. Water samples by separatory funnel extraction.

11.3.1.1. Place separatory funnels, one for each sample, in the rings attached to the separatory funnel rotator in the hood.

11.3.1.2. Place the 500 mL round bottom flasks directly beneath a powder funnel containing glass wool and sodium sulfate, which is placed beneath the separatory funnel.

11.3.1.3. Place the bottle containing the sample on a tared balance and tare the balance again. Carefully add the sample to the separatory funnel, taking care not to spill any sample. For the method blank and the OPR, use a 1000 mL graduated cylinder to measure 1000 mL of reagent water. Place the empty sample bottle back on the balance and record the difference on the extraction benchsheet. If toxaphene is requested, then a second OPR must be created for this analysis.

11.3.1.4. Add an appropriate amount of the labeled isotope dilution analyte spiking solution to the sample. For the OPR and requested Matrix Spike and Matrix Spike Duplicates, add an appropriate amount of the native compound spiking solution (add toxaphene native to the toxaphene specific OPR). Record the amount of spike used and the spike standard number in the standards logbook and on the bench sheet.

11.3.1.5. Add 100 mL of methylene chloride to the sample bottle and shake. Then add the methylene chloride to the separatory funnel.

11.3.1.6. Extract the sample by rotating the separatory funnel in the rotator for 2 minutes.

WARNING: Separatory funnel extraction with methylene chloride is a high-risk activity. Pressure may build rapidly in the funnel. It should be vented after several seconds of shaking, and often enough to prevent build-up of pressure. Chemists performing separatory funnel extraction must wear a face shield over their safety glasses/goggles. Alternatively, the extraction can be performed behind a closed fume sash.

11.3.1.7. Allow the water and the methylene chloride to separate. If it is not separated after 10 minutes, try to break up the emulsion by gently swirling the sample or tilting the separatory funnel on its side.

11.3.1.8. Drain the methylene chloride from the separatory funnel into the glass funnel that is filled with sodium sulfate. Allow the extract to drip into the round bottom flask.

11.3.1.9. Repeat steps 11.3.1.5 through 11.3.1.8 two more times.

11.3.1.10. After the third methylene chloride portion has filtered through the sodium sulfate, rinse the funnel with approximately 30 mL of methylene chloride.

11.3.1.11. Remove the separatory funnel from the hood and pour the extracted water into the extracted waters waste carboy.

11.3.1.12. Remove the glass funnel from the top of the round bottom flask, add 5 mL of hexane.

11.3.1.13. Proceed to Section 11.4 for macro concentration step.

11.3.2. Tissue Sample Pretreatment

11.3.2.1. If the sample matrix is tissue and has not been homogenized prior to sample receipt, blend the entire sample to provide a homogeneous sample.

11.3.2.2. Cut tissue into pieces of a uniform size (approximately 1 inch square). Homogenize the tissue sample in a laboratory blender or meat grinder.

11.3.2.3. Weigh out 10 grams of the homogenized tissue sample and record the weight on the sample prep sheet. Add the 10 gram sample to approximately 20 g of sodium sulfate. Mix the tissue/sodium sulfate mixture until the sample/sodium sulfate mixture is homogenized.

11.3.2.4. Proceed to Section 11.3.3 for Soxhlet extraction.

11.3.3. Solid sample extraction – Soxhlet extraction

11.3.3.1. Prepare the Soxhlet by cleaning and rinsing per Section 6.1, charging the boiling flask with solvent, assembling the components, and pre-cleaning by reflux for a minimum of 4 hours before use. Alternately the glassware can be kilned overnight and rinsed with the extraction solvent before assembly.

WARNING: Open the chiller supply valves about 15 minutes before turning of the heating element and ensure that all of the condensers are cold. Check all of the condensers about 15 minutes after starting the heating process to ensure they are still cold and functioning properly. If this cycle is to be left unattended (e.g., overnight) the first chemist to arrive the next morning is to check all condensers to ensure that they are still cold and functioning properly.

NOTE: A Dean-Stark apparatus may be used; however the water from the sample will not be removed since the water will sit on top of the extraction solvent. If used, the Dean-Stark apparatus is installed between the Soxhlet body and the condenser when the components are assembled.

WARNING: If sediment/soil samples have been frozen in glass jars, the freezing process may have cracked the jars. Wear cut protective gloves while handling the jars until it can be confirmed that they have not cracked.

11.3.3.2. For frozen samples, on the day the extraction is to be performed, remove the sample jars to be extracted from the freezer. (Record the time that they are removed.) Allow them to stand at room temperature for at least 2 hours. Once samples thaw to the point that they can be mixed, mix them and proceed as soon as possible with weighing, spiking, and extraction. Refreeze any remaining sample as soon as possible. It may take longer than 2 hours for the samples to thaw to the point that mixing and subsampling is effective, however, the extraction should begin within 8 hours of removal of the sample from the freezer.

11.3.3.3. For soil/sediment samples, weigh enough sample to achieve a nominal mass of 10 g.

NOTE: For some clients, it may be necessary to weigh enough sample to achieve a minimum of 10 g dry weight. For example if the sample has 23% moisture, weight at least 13g. Record the sample weight to the nearest 0.01 g.

NOTE: if a sample is known to contain high levels of OC pesticides or PAHs, a smaller sample size may be extracted.

11.3.3.3.1. If using pretreated tissue from Section 11.3.2, transfer the entire pretreated sample (10 g tissue + 20 g sodium sulfate) to the thimble. Record the sample weight on the sample prep sheet.

11.3.3.4. Methylene chloride rinsed sodium sulfate is used for the blank and OPR. A second OPR is created if toxaphene is requested.

11.3.3.4.1. For tissue samples, 1 g of vegetable oil or canola oil is added to the OPR. A second OPR is created if toxaphene is requested.

11.3.3.5. Spike each sample with an appropriate amount of the isotope dilution analyte solution and add a small amount of glass wool, if needed, to the top of the extraction thimble.

11.3.3.6. Spike the OPR and requested Matrix Spike and Matrix Spike Duplicates with an appropriate amount of the native spiking solutions prior to adding the glass wool. Create a second OPR if toxaphene is requested. This second OPR is spiked with isotope dilution analytes and with toxaphene spike only.

11.3.3.7. Pour approximately 350 mL of 1:1 methylene chloride:acetone into a 500 mL round bottom flask. (If toluene extraction is required use 350 ml of toluene instead of the 1:1 methylene chloride: acetone). Place the flask in the heating mantle. Add several PTFE boiling chips.

NOTE: If the samples are to be analyzed for other parameters such as PCDDs/PCDFs or PCBs the methylene chloride extraction will be followed by a toluene extraction. An aliquot from each of these extractions will be combined during sample concentration.

11.3.3.8. Place the extraction thimble in the glass Soxhlet extractor.

11.3.3.9. Assemble the Soxhlet system and secure to the lab supports.

11.3.3.10. Adjust the temperature of the heating mantle to bring the solvent in the round bottom flask to a rolling boil. There should be a steady drip from the condensers so that the solvent should completely cycle at least 5 times an hour.

WARNING: Open the chiller supply valves about 15 minutes before turning on the heating element and ensure that all of the condensers are cold before you turn the heating element on. Check all of the condensers about 15 minutes after starting the heating process to ensure that they are still cold and functioning properly. If this cycle is to be left unattended (e.g., overnight) the first chemist to arrive the next morning is to check all condensers to ensure that they are still cold and functioning properly.

11.3.3.11. Extract the sample in the above manner for 16 hours.

11.3.3.12. Turn off the heating mantle and allow to cool.

11.3.3.13. Remove the condensers and Dean Starks. Allow the Soxhlet extractor chamber to empty then remove the Soxhlet extractor from the 500 mL round bottom flask.

11.3.3.14. Add 5 mL hexane to each round bottom flask.

11.3.3.15. Proceed to Section 11.4 for macro concentration step.

11.3.4. Waste Sample Extraction

11.3.4.1. Organic wastes, oils, solids and non-aqueous sludge samples that will dissolve in solvent may be prepared by this waste dilution technique.

11.3.4.2. Add an appropriate amount of sample (e.g. 1.0 g or less) to a 40 mL VOA vial.

11.3.4.2.1. A sample dilution and aliquot may also be suitable for high organic matrices to give even a smaller sample size (e.g. 1.0 g to 40 mL solvent and take a 4.0 mL aliquot for an effective sample size of 0.1 g).

11.3.4.3. Spike the sample(s) plus QC with an appropriate amount of the isotope dilution analyte spiking solution. The QC will be a Method Blank and OPR (a second OPR if toxaphene is requested) that has 1.0 mL of the same dilution solvent used in Section 11.3.4.2.1.

11.3.4.4. Spike the OPR and requested Matrix Spikes and Matrix Spike Duplicates (MS/MSD) with an appropriate amount of native standard spiking solution. Create a second OPR if toxaphene is requested. Spike the second OPR with isotope dilution analytes and toxaphene only.

11.3.4.5. Record the weights, volumes, spike solution ID and the volume spiked on the laboratory benchsheets.

11.3.4.6. Add hexane to bring the volume to 40 mL.

11.3.4.7. Proceed to Section 11.5.

11.4. Macro Concentration

11.4.1. Place the 500 mL flask on the roto-vap.

11.4.1.1. For methylene chloride or methylene chloride/acetone concentration adjust the temperature to 60°C and do not use any vacuum.

11.4.1.2. For hexane concentration adjust the temperature to 60°C and vacuum pressure to 15 psi.

11.4.1.3. For toluene concentration adjust the temperature to 80°C and vacuum pressure to 25 psi.

11.4.2. Once the extract is concentrated down to approximately 2 mL, remove the flask from the roto-vap.

11.4.3. If proceeding to GPC, solvent exchange to methylene chloride.

11.4.4. If proceeding to silica gel, mercury, or Florisil cleanup, solvent exchange to hexane.

11.4.5. It may be necessary to archive a portion of the extract before any cleanup steps.

11.4.5.1. Transfer the extract into a 16 mL vial, rinsing the 500 mL flask 3 times with hexane. Add the rinses to the 16 mL vial. Adjust the volume to 10 mL in hexane. Remove an appropriate aliquot for processing, based upon provided screening information and other factors. Archive the remaining portion of the extract.

11.4.6. Proceed to Section 11.5.

11.5. Extract Cleanup

11.5.1. All cleanup columns may be modified based on packing material activity and elution profile. Before any cleanup column can be used, a performance based QC must show elution and activity is sufficient for the method.

11.5.2. Gel Permeation Chromatography (GPC)

11.5.2.1. This procedure is necessary for tissue samples, but may also be advantageous with other heavy organic matrices (e.g. sediments and wastes).

11.5.2.2. Concentrate and solvent exchange the sample extracts to 5 mL in methylene chloride.

11.5.2.2.1. Filter each extract through a 0.45 micron filter disk before adding to the GPC.

WARNING: Application of excessive force has, on occasion, caused a filter disc to burst during the process. Exercise caution when using syringes with attached filter assemblies.

11.5.2.2.2. If an extract is known to contain more that 1.0g of lipid, then the sample extract should be split into multiple aliquots to go through the GPC so that less than 1.0 g of lipid goes through the column on any one aliquot.

11.5.2.3. Follow procedures outlined in WS-OP-0012.

11.5.2.3.1. Use the experiment called HiRes_Pest (or equivalent) for the Organochlorine Pesticides extract.

11.5.2.3.2. Use the experiment called HiRes_Tox (or equivalent) for the toxaphene extract.

11.5.2.3.3. Concentrate the extract to approxiamately 2 mL following the procedures in Section 11.4.

11.5.2.4. Proceed to next cleanup or Section 11.6.

11.5.3. Silica Column Cleanup (Non Activated) – Using this cleanup may cause additional interferences in the 13C-Methoxyclor mass.

11.5.3.1. To a 20 mm ID column add a glass wool plug, followed by 10 g non activated silica gel followed by approximately 2 cm pre-cleaned sodium sulfate.

11.5.3.2. Pre-elute the column with approximately 2 x 20 mL DCM and discard the DCM. Blow out the column with air or N2 following each DCM rinse.

11.5.3.3. Pre-elute the column with approximately 30 mL hexane and discard the hexane. Blow out the column with air or N2 following this hexane rinse.

11.5.3.4. Add the extract in hexane with two 3 mL hexane rinses.

11.5.3.5. Place a 500 mL round bottom flask under the 20 mm column.

11.5.3.6. Elute and collect 50 mL 85:15 hexane:methylene chloride.

11.5.3.7. Elute and collect 120 mL methylene chloride.

11.5.3.8. Concentrate the extract to approximately 2 mL following the procedures in Section 11.4.

11.5.3.9. Proceed to next cleanup or to Section 11.6.

11.5.4. Silica Column Cleanup (Activated) – Using this cleanup is known to show losses of 13C-Endrin and Endrin.

11.5.4.1. To a 20 mm ID column add a glass wool plug, followed by 10 g activated silica gel followed by approximately 2 cm pre-cleaned sodium sulfate.

11.5.4.2. Pre-elute the column with approximately 50 mL hexane and discard the hexane.

11.5.4.3. Add the extract in hexane with two 3 mL hexane rinses.

11.5.4.4. Elute and discard 20 mL hexane. This fraction may be retained, based on matrix and analyst judgment.

11.5.4.5. Place a 500 mL round bottom flask under the 20 mm column.

11.5.4.6. Elute and collect 50 mL 85:15 hexane:methylene chloride.

11.5.4.7. Elute and collect 120 mL methylene chloride.

11.5.4.8. Concentrate the extract to approximately 2 mL following the procedures in Section 11.4.

11.5.4.9. Proceed to next cleanup or to Section 11.6.

11.5.5. Mercury Cleanup

11.5.5.1. It is common for pesticide samples to contain residual organic sulfur. This cleanup can be utilized before and after all other cleanups. Transfer the extract into a 16 mL test tube, rinsing the flask 3 times with hexane.

11.5.5.2. Add approximately 1 to 2 mL of mercury to the 16 mL test tube. (Take care not to spill the mercury on the bench top or floor. This step is very tricky and will take lots of practice.)

11.5.5.3. Tightly screw on the cap to the test tube.

11.5.5.4. Shake vigorously. If sulfur is present, the mercury will turn black.

11.5.5.5. Let the sample settle.

11.5.5.6. Filter the hexane portion through a pipette with glass wool into a new test tube.

11.5.5.7. Empty the used mercury into an approved and labeled mercury waste container.

11.5.5.8. Repeat steps 11.5.5.2 to 11.5.5.7 (up to 5 times) until the mercury no longer turns black.

11.5.5.9. Concentrate the extracts under a steady stream of N_2 until the extract volume is approximately 2 mL.

11.5.5.10. Proceed to next cleanup or Section 11.6.

11.5.6. Florisil Column Cleanup (Using Bakerbond pre-made Florisil cartridges).

11.5.6.1. This procedure does not require the use of a fractionated extract. The final extract will have all compounds of interest and is suitable for most sample matrices.

11.5.6.2. Packing Material and Apparatus needed:

- SPE Glass Florisil Columns (Bakerbond)

Note: Use the activated SPE Florisil columns stored in the Semi-Volatile prep oven. Activation time and temp are 16 hours at 155°C.

- SPE Manifold (Base has pressure gauge, vacuum connection tip, and column rack. Removable top has stainless steel tips attached to a port that can be opened and closed – usually there are twelve ports per manifold)
- Vacuum Pump and connection hose

WARNING: The use of vacuum systems during Florisil cartridge cleanup presents the risk of imploding glassware. All glassware used during vacuum operations must be thoroughly inspected prior to each use. Glass that is chipped, scratched, cracked, rubbed or marred in any manner must not be used under vacuum. It must be removed from service and replaced.

11.5.6.3. Rinse the top plate SPE manifold tips with hexane.

11.5.6.4. Pre-rinse the columns by attaching SPE columns to the SPE manifold and closing each of the manifold ports by twisting the port clockwise. Fill each of the columns with hexane and attach the manifold to a vacuum pump. Turn on the vacuum pump and open each one of the ports, one at a time by twisting counterclockwise, to drain the hexane through the column and into the manifold and close each port when the hexane reaches approximately 1 mm from the top of the Florisil column frit. Repeat this rinse one extra time leaving approximately 1 mm of hexane at the top of the Florisil column frit and close each port. Empty the waste hexane from the manifold by turning off the vacuum pump and removing the top plate from the manifold to empty the box.

11.5.6.5. Add 16 mL test tubes to the inside rack of the SPE manifold and transfer sample labels to the correct manifold location and replace the manifold top with each port tip inserted into each one of the test tubes.

11.5.6.6. Add extract to the column with two 2 mL hexane rinses and turn on the vacuum pump. One at a time, open each of the ports and collect the eluate into the test tubes. Close the ports when the solvent reaches 1 mm from the top of the frit.

11.5.6.7. Add 9 mL of 5% acetone/hexane by filling the column with a portion of the solvent and opening the port, then adding the remaining solvent while the sample is draining. Collect the eluate into the test tubes.

11.5.6.8. Remove the columns from the manifold ports and transfer the labels to 30 mL culture tubes. Rinse the manifold tips with hexane as described above.

11.5.6.9. Transfer the extracts from the test tubes to 30 mL culture tubes.

11.5.6.10. Repeat Sections 11.5.6.3 to 11.5.6.8 for very dirty soil samples or proceed to Silica Gel Cleanup in Section 11.5.4 or GPC Cleanup in Section 11.5.2.

11.5.6.11. If the extract is clear or known to be low in organic interferences, proceed to RS in Section 11.6.

11.6. Addition of Isotope dilution analyte (IS)

11.6.1. Concentrate the extract using a turbo evaporator to less than 1.0 mL.

11.6.2. Label flat bottomed concentration tubes with the appropriate sample IDs.

11.6.3. Add an appropriate amount of Isotope dilution analyte to each labeled concentration tube.

11.6.3.1. The standard amount of Isotope dilution analyte in dodecane is 20 ng in 200 uL.

11.6.3.2. If the extract was split after extraction then reduce the final isotope dilution analyte volume to that factor to retain appropriate reporting limits and isotope dilution analyte concentrations. For example, if the extract was split 1/2 after extraction then use 100 uL isotope dilution analyte. If the extract was split 1/4 after extraction then use 50 uL isotope dilution analyte.

11.6.4. Add the extract to the concentration tube containing the dodecane solvent and recovery standard.

11.6.5. Concentrate each extract to the volume of isotope dilution analyte that was added (the final volume will be in dodecane from the isotope dilution analyte).

11.6.5.1. The standard final volume is 200 uL.

11.7. Sample Analysis

11.7.1. Calibrate the instrument per Section 10.

11.7.2. An instrument blank or method blank must be analyzed after calibration and before client samples are analyzed as per Sections 9.6 and 9.7

11.7.3. Analyze the sample extracts under the same instrument operating conditions used to perform the instrument calibrations. Inject 1 to 2 µL into the GC/MS and acquire data until the last compound has eluted from the column.

11.7.4. Record analysis information in the instrument logbook. The following information is required:

Instrument data system filename
Lab sample identification

Additional information may be recorded in the logbook if necessary.

11.7.5. Generate ion chromatograms for the masses, listed in Table 5, which encompass the expected retention windows of the target pesticides. Calculate the results of the analysis using the procedures in Section 12.

12. CALCULATIONS/DATA REDUCTION

12.1. Qualitative Identification

An analyte is identified by retention time, the coincidence of the peak maxima on the SICP, and the isotopic ratio.

12.1.1. The retention time must be within ± 4 seconds of the expected retention time, defined as:

Equation 2

$$RT_E = (RRT_I)(RT_S)$$

Where:

RT_E = the expected retention time of the analyte or isotope dilution analytes.

RRT_{IDA} = the relative retention time of the analyte or isotope dilution analyte to the RT standard listed in Table 1 or Table 2, calculated using the analysis of the CS-3 during the most recent initial calibration.

RT_s = the retention time of the RT standard listed in Table 1 or Table 2 as observed in the analysis of the current sample.

12.1.2. The ion current response for both ions used for quantitative purposes must reach maximum simultaneously (± 2 seconds).

12.1.3. The isotopic ratio of the quantitation ions for each peak must be within the limits specified in Table 6. All ion current intensities must be ≥ 2.5 times the noise level for positive identification of a target.

12.2. Quantitation

12.2.1. Calculate the Labeled Isotope Dilution Analytes (R_{IDA}) relative to the Internal Standard according to the following equation:

Equation 3

$$R = \frac{A_{IDA} \times Q_{IS}}{A_{IS} \times RRF_{IDA} \times Q_{IDA}} \times 100\%$$

Where:

Ai_{IDA} = sum of the areas of the quantitation ions of the appropriate isotope dilution analyte.

A_{IS} = sum of the areas of the quantitation ions of the internal standard

Q_{IS} = ng of internal standard added to extract

Q_{IDA} = ng of isotope dilution analyte added to sample

RRF_{IDA} = mean relative response factor of the isotope dilution analyte from the initial calibration

12.2.2. Calculate the concentration of target pesticides according to the following equation:

Equation 4

$$\text{Concentration} = \frac{As \times Q_{IDA}}{A_{IDA} \times RRF_S \times W \times S}$$

Where:

As = sum of the areas of the quantitation ions of the compound of interest

A_{IDA} = sum of the areas of the quantitation ions of the appropriate isotope dilution analyte

Q_{IDA} = ng of isotope dilution analyte added to sample

RRF_s= mean relative response factor of compound from the initial calibration

W = amount of sample extracted (grams or liters)

S = decimal expression of percent solids (optional, if results are requested to be reported on dry weight basis)

12.2.3. Toxaphene concentration is calculated by first calculating the concentration of each of the 3 to 5 markers, using the RRF for each marker. Then concentration of the 3 to 5 markers are averaged to calculate the concentration of toxaphene in the sample. This approach will allow degraded toxaphene to still be correctly identified and accurately quantitated. The determination of toxaphene is not based on ion ratio, but determined by detection, pattern recognition of both ions and expected retention time of the marker peaks from the labeled isotope dilution analyte.

12.2.4. If no peaks are present (or less than 3 peaks are present in the toxaphene analysis) in the region of the ion chromatogram where the compound of interest is expected to elute, calculate the estimated detection limit (EDL) for that compound according to the following equation (for toxaphene calculate the average EDL using the 3 to 5 RRFs):

Equation 5

$$EDL = \frac{N \times 2.5 \times Q_{IDA}}{H_{IDA} \times RRFs \times W \times S}$$

Where:

- N = peak to peak noise of quantitation ion signal in the region of the ion chromatogram where the compound of interest is expected to elute
- H_{IDA} = peak height of quantitation ion for appropriate isotope dilution analyte
- Q_{IDA} = ng of isotope dilution analyte added to sample
- RRF_s = mean relative response factor of compound from the initial calibration.
- W = amount of sample extracted (grams or liters)
- S = decimal expression of percent solids (optional, if results are requested to be reported on dry weight basis)

12.2.5. If peaks are present in the region of the ion chromatogram which do not meet the qualitative criteria listed in Section 12.1, calculate an Estimated Maximum Possible Concentration (EMPC) using the equation in Section 12.2.2, except that As should represent the sum of the area under the one peak and of the other peak area calculated using the theoretical chlorine isotope ratio. The peak selected to calculate the theoretical area should be the one which gives the lower of the two possible results (i.e. the EMPC will always be lower than the result calculated from the uncorrected areas).

12.2.6. If the concentration in the final extract of any pesticide exceeds the upper method calibration limits, a dilution of the extract or a re-extraction of a smaller portion may be performed if deemed necessary by the client. Otherwise the results shall be flagged with an “E” qualifier denoting it as exceeding the upper calibration range. If a compound concentration saturates the detector a dilution shall be performed in an attempt to bring the impacted isomer within the detector’s limit. Re-extraction of a smaller aliquot or a post spike dilution may be necessary, and shall be performed upon consultation with the client.

12.2.7. The Minimum Level (ML) is defined as the level at which the instrument gives acceptable calibration assuming a sample is extracted at the recommended weight or volume and is carried through all normal extraction and analysis procedures. Deviation from the extraction amounts or final volumes listed in Table 3 may change the ML.

12.3. Data Flagging

12.3.1. Flag all compound results in the sample which were detected in the method blank with a “B” qualifier.

12.3.2. Flag all compound results in the sample which are below the lower calibration level with a “J” qualifier.

12.3.3. Flag all compound results in the sample which are above the upper calibration limit with an “E” qualifier.

12.3.4. Flag all compound results in the sample which are “Estimated Maximum Possible Concentrations” with a “Q” or “JA” qualifier, per client requirement.

12.3.5. Flag all compound results in the sample which have elevated reporting limits due to elevated noise versus the reporting limit with a “G” qualifier, per client requirements.

12.4. Data review

12.4.1. The analyst who performs the qualitative and quantitative analysis on the sample data must initial and date the front quantitation sheet of the raw data.

12.4.2. A second analyst must verify all qualitative peak identifications. If discrepancies are found, the data must be returned to the analyst who performed the initial peak identification for resolution.

12.4.3. A second analyst must check all hand calculation(s) and data entry into calculation programs, databases, or spreadsheets at a frequency of 100 percent. If discrepancies are found, the data must be returned to the analyst who performed the initial calculation for resolution.

12.4.4. The analyst who performs the second level review on the sample data must initial and date any corrections to the raw data package.

12.4.5. Both the analyst who performed the initial qualitative and quantitative analysis and the analyst who performed the second level review must check all items listed on the data review checklist and initial and date the checklist.

13. METHOD PERFORMANCE

13.1. Method Detection Limit

Each laboratory must generate a valid method detection limit for each analyte of interest. The MDL must be below the reporting limit for each analyte. The procedure for determination of the method detection limit is given in 40 CFR Part 136, Appendix

B, and further defined in SAC-QA-0006. The MDL is available in the Quality Assurance department.

13.2. Initial Demonstration

Each laboratory must make a one time initial demonstration of capability for each individual method. Demonstration of capability for both soils and water matrices is required. This requires analysis of QC check samples containing all of the standard analytes for the method. For some tests it may be necessary to use more than one QC check mix to cover all analytes of interest.

13.2.1. Initial precision and recovery (IPR) - To establish the ability to generate acceptable precision and recovery, the analyst shall perform the following operations.

13.2.2. Four aliquots of the QC check sample are analyzed using the same procedures used to analyze samples, including sample preparation. The concentration of the QC check sample should be equivalent to a mid level calibration.

13.2.3. Calculate the average recovery and standard deviation of the recovery for each analyte of interest. Compare these results with the acceptance criteria given in Table 8.

13.2.4. If any analyte does not meet the acceptance criteria, the test must be repeated. Only those analytes that did not meet criteria in the first test need to be evaluated. Repeated failure for any analyte indicates the need for the laboratory to evaluate the analytical procedure and take corrective action.

13.3. Training Qualification

The department manager/supervisor has the responsibility to ensure that this procedure is performed by an analyst who has been properly trained in its use and has the required experience.

14. POLLUTION PREVENTION

It is TestAmerica's policy to evaluate each method and look for opportunities to minimize waste generated (i.e., examine recycling options, ordering chemicals based on quantity needed, preparation of reagents based on anticipated usage and reagent stability). Employees must abide by the policies in Section 13 of the Corporate Environmental Health and Safety Manual (CW-E-M-001) for "Waste Management and Pollution Prevention."

14.1. All waste will be disposed of in accordance with Federal, State and Local regulations. Where reasonably feasible, technological changes have been implemented to minimize the potential for pollution of the environment

14.2. Do not allow waste solvent to evaporate in fume hoods. All solvent waste is stored in capped containers unless transfers are being made.

14.3. The use of roto-vaps and turbo-vaps rather than Kuderna-Danish reduction allows extraction solvents to be collected and disposed of rather than released to the atmosphere.

15. WASTE MANAGEMENT

Waste management practices are conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes are disposed of in an accepted manner. Waste description rules and land disposal restrictions are followed. Waste disposal procedures are incorporated by reference to SOP WS-EHS-0001. The following waste streams are produced when this method is carried out.

15.1. Extracted aqueous samples contaminated with methylene chloride are collected at the fume hood in a 5-gallon or smaller carboy. If the samples are not at a neutral pH, add small quantities of sodium bicarbonate to bring the waste to neutral. Stir well. Once neutralized, immediately pour the carboy contents into a blue plastic LLE drum in the H3 closet. When full to between one and four inches of the top, or after no more than 75 days, move the LLE drum to the waste collection area for shipment.

15.2. Extracted soil, resin and tissue samples, thimbles, used florisil cartridges and silica gel columns, used used sodium sulfate and glass wool contaminated with various solvents. Dump the materials into an orange contaminated soil bucket. When the bucket is full or at the end of the day, whichever comes first, tie the plastic bag liner shut and put the lab trash into the appropriate steel collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.3. Used bench paper, gloves and lab materials that may or may not be contaminated. Put the materialsl into a yellow contaminated lab trash bucket. When the bucket is full or after no more than one year, tie the plastic bag liner shut and put the lab trash into the appropriate steel collection drum in the H3 closet. When the drum is full or after no more than 75 days, move it to the waste collection area for shipment.

15.4. Used mercury contaminated with sulfur compounds from the sulfur cleanup. Pour the contaminated mercury into a 250 mL plastic bottle labeled for contaminated mercury. When full or after no more than one year, whichever comes first, transfer this jar to the waste collection area for shipment.

15.5. Assorted flammable solvent and methylene chloride waste from various rinses or pre-elutions. Collect the waste solvents in tripours during use. Empty the tripours into a 1-liter to 4-liter carboy at the fume hood. When the carboy is full, or at the end of your shift, whichever comes first, empty the carboy into the steel solvent drum in the H3 closet. When full to between two and six inches of the top, or after no more than 75 days, move the steel drum to the waste collection area for shipment.

16. REFERENCES/CROSS REFERENCES

16.1. NYSDEC Draft Method HRMS-2: Analytical Procedures for Organochlorine Pesticides by Isotope Dilution HRGC/HRMS. Feb. 1999 Draft.

16.2. NYSDEC Draft Method HRMS-2: Analytical Procedures for Organochlorine Pesticides by Isotope Dilution HRGC/HRMS. Feb. 2004 Draft.

16.3. EPA Method 1668, Revision A, December, 1999, "Chlorinated Biphenyl Congeners in Water, Soil, Sediment, and Tissue by HRGC/HRMS".

16.4. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, Update III, Method 3620B, Revision 2, December 1996, "Florisil Cleanup".

16.5. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, Update III, Method 8290, Revision 0, September 1994, "Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS)".

16.6. EPA Method 680, November 1985, "Determination of Pesticides and PCB's in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry".

16.7. SW846, Test Methods for Evaluating Solid Waste, 3rd Edition, Update III, Method 8081A, Revision 1, December 1996, "Organochlorine Pesticides by Gas Chromatography".

16.8. Method 1699, Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, December 2007.

17. METHOD MODIFICATIONS

17.1. Deviations from reference method (NYSDEC HRMS-2)

17.1.1. Added additional cleanup options.

17.1.2. Added additional isotope dilution analytes.

17.1.3. Added additional internal standards.

17.2. Deviations from Reference Method EPA 1699

17.2.1. TestAmerica Sacramento utilizes a 5 point calibration rather than a 6 point calibration as listed in Table 4 of Method 1699.

17.2.2. TestAmerica Sacramento uses a modification to Method 1699 for evaluating the breakdown of DDT (Section 9.5).

18. ATTACHMENTS

18.1. Table 1 — Analytes and Corresponding Isotope Dilution Analytes

18.2. Table 2 — Isotope Dilution Analytes and Corresponding Internal Standards

18.3. Table 3 — Types of Matrices, Sample Sizes, and Typical Method Calibration Limits

18.4. Table 4 — Concentrations of Calibration Standards (ng/mL)

18.5. Table 5 — Ions Monitored for HRGC/HRMS Analysis of Organochlorine Pesticides

18.6. Table 6 — Theoretical Ion Abundance Ratio Control Limits for Pesticides

18.7. Table 7 — OPR Spiking Components, Concentrations and QC Limits

18.8. Table 8 — IPR/VER Acceptance Criteria

18.9. Figure 1 — Typical Retention Times

19. REVISION HISTORY

19.1. WS-ID-0014 rev. 5.9, Effective Date 10/31/2014

19.1.1. Section 11.3.3.3 – replaced sentence from "weigh enough sample to achieve a nominal mass of 10g" to "weigh enough sample to achieve a nominal mass of 1.0g" and changed weight amounts in NOTE following Section 11.3.3.3 from 1.0g to 1.-g and from 13g to 1.3g.

19.1.2. Section 11.3.3.3.1 – replaced parenthesized sentence from "(10g tissue + 20g sodium sulfate)" to "(1g tissue _ 2g sodium sulfate)".

19.1.3. Section 11.3.3.4.1 – replaced "For tissue samples, 1.0g of vegetable oil or canola oil is added to the OPR." to "For tissue samples, 0.25g of vegetable oil or canola oil is added to the OPR."

19.1.4. Table 3 – changed 1-0g to 1g under Soil and Tissue headings.

19.1.5. Editorial changes.

19.1.6. Updated Proprietary Statement 08/27/2015.

19.2. WS-ID-0014 rev. 5.8, Effective Date 06/06/2014

19.2.1. Deleted from Section 10.3.6 - "Endrin aldehyde and endrin ketone do not have unlabelled isotope dilution analytes, so the RSD for the mean RRF should not exceed 35% for these analytes."

19.2.2. Deleted $^{13}C_{12}$ Tetrachlorobiphenyl (70) from Retention Time and Internal Standard list in Table 2.

19.2.3. Inserted ^{13}C-Hexachlorobipheny (138) to Internal Standard section of Table 4.

19.2.4. Deleted ^{13}C-Decachlorobiphenyl (202) from Isotope Dilution Analyte list in Table 7.

19.2.5. Inserted Section 17.2 – Deviations from Reference Method EPA 1699 and appended Section(s) 17.2.1 and 17.2.2.

19.2.6. Editorial changes.

19.3. WS-ID-0014, Revision 5.7, Effective Date 04/26/2013

19.3.1. Changed definitions of internal standards to isotope dilution analytes, and recovery standards to internal standards to match definitions in method.

19.3.2. Editorial changes.

19.4. WS-ID-0014, Revision 5.6, Effective Date 02/10/20152/

19.4.1. Inserted Section 6.5: "This laboratory operates an Agilent GC 7890A GC and Autospec Premier mass spec which utilizes a Masslynx v4.1 software or equivalent."

19.4.2. Editorial changes.

19.5. WD-ID-0014, Revision 5.5, Effective Date 09/09/2011

19.5.1. Modified Tables 1 – 8 to include $^{13}C_{12}$ Endrin aldehyde and $^{13}C_{11}$ Endrin ketone.

19.5.2. Updated Figure 1: Typical Retention Time Summary Report.

19.6. WS-ID-0014 Revision 5.4, Effective Date 08/11/2011

19.6.1. Modified Sections 2.1.2; 5.2; 7.5; 11.7,3.7; 11.4.1.3; and 15.2 to reflect the option for toluene extraction.

19.7. WS-ID-0014 Revision 5.3, Effective Date 11/17/2010

19.7.1. Removed Sections 11.5.3.4 and 11.5.3.6.

Table 1
Analytes and Corresponding Isotope Dilution Analytes

Analyte	CAS Registry Number	Retention Time / Isotope Dilution Analytes	CAS Registry Number
Aldrin	309-00-2	$^{13}C_{12}$-Aldrin	309-00-2L
alpha-BHC	319-84-6	$^{13}C_{6}$-alpha-BHC	319-84-6L
beta-BHC	319-85-7	$^{13}C_{6}$-beta-BHC	319-85-7L
gamma-BHC	58-89-9	$^{13}C_{6}$-gamma-BHC	58-89-9L
delta-BHC	319-86-8	$^{13}C_{6}$-delta-BHC	319-86-8L
cis-Chlordane	5103-71-9	$^{13}C_{10}$-cis-Chlordane	5103-71-9L
trans-Chlordane	5103-74-2	$^{13}C_{10}$-trans-Chlordane	5103-74-2L
oxy-Chlordane	27304-13-8	$^{13}C_{10}$-oxy-Chlordane	27304-13-8L
2,4'-DDD	53-19-0	$^{13}C_{12}$-2,4'-DDD	53-19-0L
4,4'-DDD	72-54-8	$^{13}C_{12}$-4,4'-DDD	72-54-8L
2,4'-DDE	3424-82-6	$^{13}C_{12}$-2,4'-DDE	3424-82-6L
4,4'-DDE	72-55-9	$^{13}C_{12}$-4,4'-DDE	72-55-9L
2,4'-DDT	784-02-6	$^{13}C_{12}$-2,4'-DDT	784-02-6L
4,4'-DDT	50-29-3	$^{13}C_{12}$-4,4'-DDT	50-29-3L
Dieldrin	60-57-1	$^{13}C_{12}$-Dieldrin	60-57-1L
Endosulfan I	959-98-8	$^{13}C_{9}$-Endosulfan I	959-98-8L
Endosulfan II	33212-65-9	$^{13}C_{9}$-Endosulfan II	33212-65-9L
Endosulfan sulfate	1031-07-8	$^{13}C_{9}$-Endosulfan sulfate	1031-07-8L
Endrin	72-20-8	$^{13}C_{12}$-Endrin	72-20-8L
Endrin Aldehyde	7421-36-3	$^{13}C_{12}$-Endrin Aldehyde	7421-36-3L
Endrin Ketone	53494-70-5	$^{13}C_{11}$-Endrin Ketone	53494-70-5L
Heptachlor	76-44-8	$^{13}C_{10}$-Heptachlor	76-44-8L

Heptachlor epoxide B	1024-57-3	$^{13}C_{12}$-Heptachlor epoxide B	1024-57-3L
Hexachlorobenzene	118-74-1	$^{13}C_{6}$-Hexachlorobenzene	118-74-1L
Methoxychlor	72-43-5	$^{13}C_{12}$-Methoxychlor	72-43-5L
Mirex	2385-85-5	$^{13}C_{10}$-Mirex	2385-85-5L
cis-Nonachlor	5103-73-1	$^{13}C_{10}$-cis-Nonachlor	5103-73-1L
trans-Nonachlor	39765-80-5	$^{13}C_{10}$-trans-Nonachlor	39765-80-5L
Toxaphene*	8001-35-2	$^{13}C_{6}$-alpha-BHC	319-84-6L

*Toxaphene is a group of peaks within a retention time window specified by the "toxaphene" standard and second source.

Note: Alternative isotope dilution analytes may be assigned as appropriate.

Table 2
Isotope Dilution Analytes and Corresponding Internal Standards

Isotope Dilution Analytes	Retention Time and Internal Standard
$^{13}C_6$-alpha-BHC	$^{13}C_{12}$-Dichlorobiphenyl (15)
$^{13}C_6$-beta-BHC	
$^{13}C_6$-gamma-BHC	
$^{13}C_6$-delta-BHC	
$^{13}C_6$-Hexachlorobenzene	
$^{13}C_{10}$-Heptachlor	
$^{13}C_{12}$-Aldrin	$^{13}C_{12}$-Tetrachlorobiphenyl (52)
$^{13}C_{10}$-oxy-Chlordane	
$^{13}C_{10}$-Heptachlor epoxide B	
$^{13}C_{12}$-2,4'-DDE	$^{13}C_{12}$-Pentachlorobiphenyl (101)
$^{13}C_9$-Endosulfan I	
$^{13}C_{10}$-trans-Chlordane	
$^{13}C_{10}$-cis-Chlordane	
$^{13}C_{10}$-trans-Nonachlor	
$^{13}C_{12}$-2,4'-DDD	$^{13}C_{12}$-Hexachlorobiphenyl (138)
$^{13}C_{12}$-4,4'-DDE	
$^{13}C_{12}$-4,4'-DDD	
$^{13}C_{10}$-cis-Nonachlor	
$^{13}C_{12}$-2,4'-DDT	
$^{13}C_{12}$-4,4'-DDT	
$^{13}C_9$-Endosulfan sulfate	
$^{13}C_{10}$-Mirex	
$^{13}C_{12}$-Dieldrin	
$^{13}C_{12}$-Endrin	
$^{13}C_9$-Endosulfan II	
$^{13}C_{12}$-Methoxychlor	
$^{13}C_{12}$-Endrin Aldehyde	
$^{13}C_{11}$-Endrin Ketone	

Table 3
Types of Matrices, Sample Sizes and Typical Method Calibration Limits
Single Eluting Pesticides

	Water (ng/L)	Solid (ng/g)	Tissue (ng/g)	Wipe (ng)	XAD (ng)	Waste (ng/g)
Lower MCL	0.4- 2	0.04- 0.2	0.04- 0.2	0.4- 0.2	0.4-0.2	4.0-20
Upper MCL	200	20	20	200	200	2000
I.S. Spike	10	1.0	1.0	10	10	100
Sample Size (L or g)	1 L	10 g	10 g	Entire Sample	Entire Sample	0.1g
OPR Spiking Levels	20.0	2.0	2.0	20.0	20.0	200
R.S. Spike	20	2	2	20	20	200
Final Extract Vol. (µL)	200	200	200	200	200	200

Note: The lower MCL applies to most target pesticides. Some target compounds elicit reduced instrument response due to fragmentation. A range of minimum calibration limits is specified to reflect the possibly that CS1 may be dropped from the calibration for these compounds. The reporting limit for endosulfan I is 5 times higher than other pesticides due to increased background noise for this analyte.

Note: Final volume may be reduced to account for sample splitting after extraction.

Table 3A

Types of Matrices, Sample Sizes and Typical Method Calibration Limits for Toxaphene

	Water (ug/L)	Solid (ug/g)	Tissue (ug/g)	Wipe (ug)	XAD (ug)	Waste (ug/g)
Lower MCL	0.1	0.01	0.01	0.1	0.1	1.0
Upper MCL	20	2.0	2.0	20	20	200
I.S. Spike	10	1.0	1.0	10	10	100
Sample Size (L or g)	1 L	10 g	10 g	Entire Sample	Entire Sample	0.1 g
OPR Spiking Levels	4.0	0.4	0.4	4.0	4.0	40
R.S. Spike	20	2.0	2.0	20	20	200
Final Extract Vol. (µL)	200	200	200	200	200	200

Note: Final volume may be reduced to account for sample splitting after extraction.

Table 4
Concentrations of Calibration Standards for Organochlorine Pesticides (ng/mL)

Analyte	CS1 *	CS2	CS3	CS4	CS5	CS6	CS7
Aldrin	1	2	10	50	200	500	1000
alpha-BHC	1	2	10	50	200	500	1000
beta-BHC	1	2	10	50	200	500	1000
delta-BHC	1	2	10	50	200	500	1000
gamma-BHC	1	2	10	50	200	500	1000
cis-Chlordane	1	2	10	50	200	500	1000
trans-Chlordane	1	2	10	50	200	500	1000
oxy-Chlordane	1	2	10	50	200	500	1000
Dieldrin	1	2	10	50	200	500	1000
2,4'-DDD	1	2	10	50	200	500	1000
4,4'-DDD	1	2	10	50	200	500	1000
2,4'-DDE	1	2	10	50	200	500	1000
4,4'-DDE	1	2	10	50	200	500	1000
2,4'-DDT	1	2	10	50	200	500	1000
4,4'-DDT	1	2	10	50	200	500	1000
Endosulfan I	1	2	10	50	200	500	1000
Endosulfan II	1	2	10	50	200	500	1000
Endosulfan sulfate	1	2	10	50	200	500	1000
Endrin	1	2	10	50	200	500	1000
Endrin aldehyde	1	2	10	50	200	500	1000
Endrin ketone	1	2	10	50	200	500	1000
Heptachlor	1	2	10	50	200	500	1000
Heptachlor epoxide B	1	2	10	50	200	500	1000
Hexachlorobenzene	1	2	10	50	200	500	1000
Methoxychlor	1	2	10	50	200	500	1000
Mirex	1	2	10	50	200	500	1000
cis-Nonachlor	1	2	10	50	200	500	1000
trans-Nonachlor	1	2	10	50	200	500	1000
Isotope Dilution Analytes							
$^{13}C_{12}$-Aldrin	100	100	100	100	100	100	100
$^{13}C_{6}$-alpha-BHC	100	100	100	100	100	100	100
$^{13}C_{6}$-beta-BHC	100	100	100	100	100	100	100
$^{13}C_{6}$-delta-BHC	100	100	100	100	100	100	100
$^{13}C_{6}$-gamma-BHC	100	100	100	100	100	100	100
$^{13}C_{10}$-cis-Chlordane	100	100	100	100	100	100	100
$^{13}C_{10}$-trans-Chlordane	100	100	100	100	100	100	100
$^{13}C_{10}$-oxy-Chlordane	100	100	100	100	100	100	100
$^{13}C_{12}$-Dieldrin	100	100	100	100	100	100	100
$^{13}C_{12}$-2,4'-DDD	100	100	100	100	100	100	100
$^{13}C_{12}$-4,4'-DDD	100	100	100	100	100	100	100
$^{13}C_{12}$-2,4'-DDE	100	100	100	100	100	100	100
$^{13}C_{12}$-4,4'-DDE	100	100	100	100	100	100	100
$^{13}C_{12}$-2,4'-DDT	100	100	100	100	100	100	100
$^{13}C_{12}$-4,4'-DDT	100	100	100	100	100	100	100
$^{13}C_{9}$-Endosulfan I	100	100	100	100	100	100	100
$^{13}C_{9}$-Endosulfan II	100	100	100	100	100	100	100
$^{13}C_{9}$-Endosulfan sulfate	100	100	100	100	100	100	100

Table 4
Concentrations of Calibration Standards for Organochlorine Pesticides (ng/mL)

Analyte	CS1 *	CS2	CS3	CS4	CS5	CS6	CS7
$^{13}C_{12}$-Endrin	100	100	100	100	100	100	100
$^{13}C_{10}$-Heptachlor	100	100	100	100	100	100	100
$^{13}C_{10}$-Heptachlor epoxide	100	100	100	100	100	100	100
$^{13}C_{6}$-Hexachlorobenzene	100	100	100	100	100	100	100
$^{13}C_{12}$-Methoxychlor	100	100	100	100	100	100	100
$^{13}C_{10}$-Mirex	100	100	100	100	100	100	100
$^{13}C_{10}$-trans-Nonachlor	100	100	100	100	100	100	100
$^{13}C_{10}$-oxy-Chlordane	100	100	100	100	100	100	100
$^{13}C_{12}$-Endrin Aldehyde	100	100	100	100	100	100	100
$^{13}C_{11}$Endrin Ketone	100	100	100	100	100	100	100
Internal Standards							
$^{13}C_{12}$-Dichlorobiphenyl (15)	100	100	100	100	100	100	100
$^{13}C_{12}$-Tetrachlorobiphenyl (52)	100	100	100	100	100	100	100
$^{13}C_{12}$-Tetrachlorobiphenyl (70)	100	100	100	100	100	100	100
$^{13}C_{12}$-Pentachlorobiphenyl (101)	100	100	100	100	100	100	100
^{13}C-Hexachlorobiphenyl (138)	100	100	100	100	100	100	100

NOTE: *(1 pg/µl) or 1 ng/ml may be used only as a sensitivity check standard and may not be included in ICAL calculations. If this concentration is not used then the reporting limits are based on CS2 for the analyte(s).

The lower calibration level for endosulfan I may be dropped due to excessive background noise at the lower level. Reporting limits are based on CS3 for this analyte.

Table 4A
Concentrations of Calibration Standards for Toxaphene (ng/mL)

Analyte	CS1 *	CS2	CS3	CS4	CS5	CS6	CS7
Toxaphene	100	500	1,000	5,000	20,000	50,000	100,000
Isotope Dilution Analyte							
$^{13}C_{6}$-alpha-BHC	100	100	100	100	100	100	100
Internal Standards							
$^{13}C_{12}$-Dichlorobiphenyl (15)	100	100	100	100	100	100	100

Table 5
Ions Monitored for HRGC/HRMS Analysis of Organochlorine Pesticides

Descriptor	Accurate Mass	Analyte
	234.0406	$^{13}C_{12}$-DiCB (15) [RS]
	236.0376	$^{13}C_{12}$-DiCB (15) [RS]
	230.98563	PFK QC Mass
	216.9145	BHC
	218.9116	BHC
	222.9347	$^{13}C_{6}$- BHC [IS]
	224.9317	$^{13}C_{6}$- BHC [IS]
1	271.8102	Heptachlor
	273.8072	Heptachlor
	276.8270	$^{13}C_{10}$-Heptachlor [IS]
	278.8240	$^{13}C_{10}$-Heptachlor [IS]
	283.8107	Hexachlorobenzene
	285.8072	Hexachlorobenzene
	289.8303	$^{13}C_{6}$-Hexachlorobenzene [IS]
	291.8273	$^{13}C_{6}$-Hexachlorobenzene [IS]
	301.9626	$^{13}C_{12}$-TetraCB (52) [RS] $^{13}C_{12}$-TetraCB (70) [RS]
	303.9597	$^{13}C_{12}$-PentaCB (52) [RS] $^{13}C_{12}$-PentaCB (70) [RS]
	280.98244	PFK QC Mass
	262.8570	Aldrin
	264.8540	Aldrin
	269.8805	$^{13}C_{10}$-Aldrin [IS]
2	271.8775	$^{13}C_{10}$-Aldrin [IS]
	386.8052	Chlordane (oxy)
	388.8023	Chlordane (oxy)
	396.8388	$^{13}C_{10}$-Chlordane (oxy) [IS]
	398.8358	$^{13}C_{10}$-Chlordane (oxy) [IS]
	352.8442	Heptachlor epoxide B
	354.8413	Heptachlor epoxide B
	362.8778	$^{13}C_{10}$- Heptachlor epoxide B [IS]
	364.8748	$^{13}C_{10}$- Heptachlor epoxide B [IS]
3	335.9236	$^{13}C_{12}$-PentaCB (101) [RS]
	337.9207	$^{13}C_{12}$-PentaCB (101) [RS]
	280.98244	PFK QC Check
	246.0003	2,4'-DDE
	247.9974	2,4'-DDE
	258.0406	$^{13}C_{12}$-2,4'-DDE [IS]
	260.0376	$^{13}C_{12}$-2,4'-DDE [IS]
	262.8570	Endosulfan I
	264.8540	Endosulfan I
	269.8805	$^{13}C_{9}$- Endosulfan I [IS]
	271.8775	$^{13}C_{9}$- Endosulfan I [IS]
	271.8102	Chlordane (cis & trans) Nonachlor (trans) Endosulfan I *

QAPP WORKSHEET NO. 33 – QA MANAGEMENT REPORTS TABLE

Reports for a variety of quality-related activities will be provided to scientists and managers at appropriate levels of the project organization. Reports include data records provided to the FOL, Task Lead, QA Lead, PMs, and agency representatives.

A summary of field and project reports is presented below:

QC Report Type	Generated By	Distributed To	Frequency
Field Instrument Calibration	Field Technicians	Field Operations Lead	Daily during sampling event
Sample FDRs	Field Technicians	Field Operations Lead	Per sample
Offsite Lab Analytical Documentation	Subcontractor	Amec Foster Wheeler QA Lead	Project specified
Data Validation Report	Amec Foster Wheeler QA Lead (or designated representative)	Included in Report	Each investigation
Investigation Reports (RD/RAWP Addendum)	PM/Authors	Amec Foster Wheeler, EPA, ADEQ	One – at completion, see below
Laboratory Audit Report	Amec Foster Wheeler QA Lead	Project Team	Not expected during the duration of this work
Corrective Action	Any Team Member	Project Team	As needed

Notes:
ADEQ – Arizona Department of Environmental Quality
EPA – U.S. Environmental Protection Agency
FDR – field and data records
PM – Project Manager
QA – Quality Assurance

Project Deliverables

This addendum will be submitted to AFCEC for review, and revisions resulting from this review will be incorporated into the draft report to be reviewed by EPA, ADEQ, and other interested parties, if required. Following agreement on comments, a final report addendum will be prepared and submitted.

EBR operational data will be made available and will be formally presented in the form of quarterly O&M reports.

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